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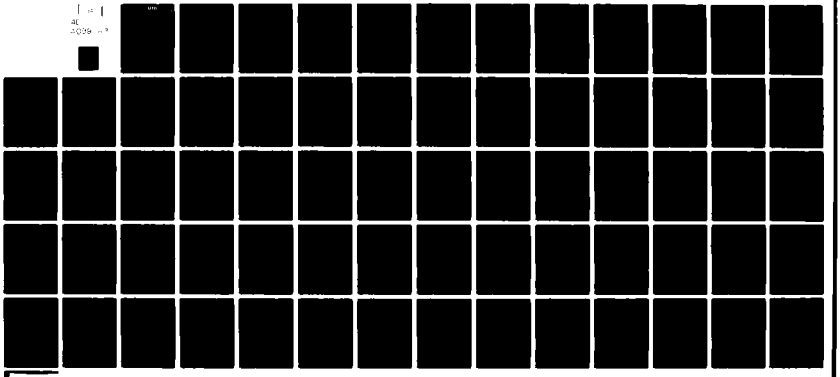

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This report summarizes research under this Grant to develop new theoretical and computational methods for studying the properties of materials. In particular, it describes the use of ab initio methods to predict (a) chemical bonding in systems composed of heavy elements, (b) relativistic effects in molecules, and (c) relativistic calculation of core-electron (x-ray) ionization spectra and related effects.

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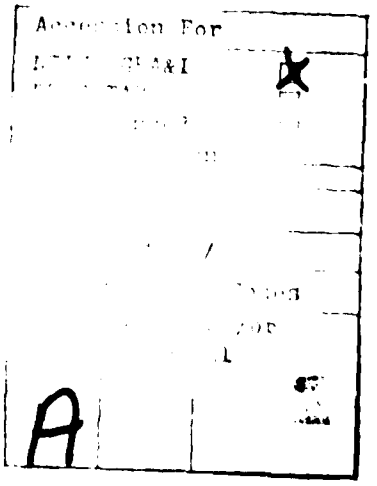

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ABSTRACT

Research under this Grant has developed new theoretical and computational methods for studying the properties of materials. In particular, it has addressed the problems of using *ab initio* computations to predict (a) chemical bonding in systems composed of heavy elements, (b) relativistic effects in molecules, and (c) core-electron spectra, such as obtained by XPS experiments, in heavy atoms and molecules. Practical computational techniques have been formulated and tested which allow not only improved understanding of the theory of materials, but also routine calculations of energies and structures of a variety of atomic and molecular systems.

AFOSR 77-3145

DEVELOPMENT & PRACTICAL APPLICATION OF THE THEORY OF MATERIALS

I. Introduction

Any Air Force which does not keep its doctrines ahead of its equipment and its visions far into the future can only delude the nation into a false sense of security.

General H. H. Arnold

The research carried out under Grant AFOSR-77-3145 has examined some of the most basic principles governing the ways in which materials are composed in terms of atoms and molecules. Our first objective was to pursue the concept of core electrons, which are of comparatively high energy and do not participate directly in bonding between atoms, as opposed to the lower-energy valence elctrons that do tend to form bonds. This distinction allows extremely efficient *ab initio* computational methods for the calculation of molecular structure, such as the NOCOR procedure we developed during the previous Grant period. For example, we have shown that an increase in computational efficiency of roughly an order of magnitude for molecules composed of elements from successive rows of the Periodic Table may result.

Our original method was largely limited to nonrelativistic single-configuration calculations using simple basis sets to describe the electron distributions. This was found to be a surprisingly accurate way of describing relatively large molecular systems composed of moderately heavy elements, such as phosphorus, silicon and germanium. However during the present Grant period we have extended both the theory and computer programs to make the procedure much more general. Thus it is now applicable to any set of basis functions, either single- or multiconfiguration calculations, species with unpaired electrons, and has the facility to treat relativistic effects, which predominate in many properties of heavy elements such as lead and uranium. Thus we have now developed a computational tool for predicting a variety of spectroscopic and chemical properties.

A number of discoveries in related fields were an outgrowth of this effort. From a theoretical viewpoint, by far the most significant was the development of the first completely relativistic theory of molecular structure, along with the associated computer programs. For this we have employed the self-consistent-field approach using the Dirac (relativistic) equation of electron motion. Implementation of the Dirac equation involved considerable computational complexity, since all orbitals are four-component complex functions instead of one-component real functions as in the nonrelativistic approximation. Although our program is presently at a level only analogous to the restricted Hartree-Fock method, we believe it may well provide a cornerstone of subsequent work in other laboratories on the theoretical chemistry of heavy elements. Relativistic effects are now known to be quite significant in determining the chemical properties of elements from the fifth and lower rows of the Periodic Table. For example, the (relativistic) spin-orbit energies of lead compounds are often greater than their bond energies. Therefore an *ab initio* technique for predicting such effects is of central importance to work in this field.

Another outgrowth of our study of core electron properties and relativistic corrections was a procedure for calculating high-energy ionization spectra, such as X-ray photoelectron spectra (XPS), of atoms. This type of spectroscopy measures the minimal energy required to remove an electron from a core orbital. We found that employing previously-developed Dirac-Fock techniques for atoms, a striking agreement with the available experimental results could be attained. For example, differences between theory and experiment are often only 3% of the lowest errors previously reported - an error which approaches the experimental linewidth. We have now found this agreement to be consistent for core electrons with experimentally accessible energies throughout the Periodic Table.

These are the three principal areas to which we have made contributions during the tenure of this Grant. Others, which have evolved from our implementation of general-purpose *ab initio* programs, will be discussed below. In the following sections we will very briefly review the work published under this Grant. We then summarize work that has been completed but not yet published, and our conclusions. In the Appendix are some selected papers that represent the central theoretical and conceptual achievements under this Grant.

II. Summary of Work Published Under This Grant

A. Theoretical Advances

As we applied our original NOCOR approach to systems composed of increasingly unusual and heavy elements, it soon became apparent that we would have to confront the problem of relativistic effects - *i.e.* those embodied in the special theory of relativity and manifested due to the high velocity of core electrons in the region of space near a nucleus of high nuclear charge. These types of terms affect essentially every type of molecular property, including bond lengths and heats of formation. At the time we began this work, it was not known how large these effects would be. However we and others have subsequently shown that they can be significant in systems of practical interest. Our first paper on this subject[1] showed how our NOCOR procedure has a precise and theoretically rigorous analog in the Dirac-Fock formalism. We proved the interesting result that all electrostatic terms coupling core and valence orbitals in the effective core potential vanish except for one (small) term. We developed a Dirac-Fock procedure for calculating valence-only molecular properties under the assumption that only core electrons move at relativistic velocities. Finally, we showed how a practical computational procedure using this approach could be developed, and reported sample calculations on the spectroscopic properties of the PbO molecule. In this compound, since there is only one heavy element, the relativistic shift is fairly modest: about 0.01 Å in the bond length and 10 cm^{-1} in the vibrational frequency. A copy of this paper is included below as Appendix A.

Our next paper[2] in this series dealt with the formation of effective potentials at a basic theoretical level. We demonstrated how our effective potential procedure could be extended to a somewhat higher level of accuracy by employing distinct core potentials for each valence orbital. This in turn allows the construction of rigorous Phillips-Kleinman pseudopotentials for systems with unpaired electrons and , more importantly, for the case of configuration mixing. For the latter we have developed an effective-potential multiconfiguration SCF program. This procedure allows the calculation of all molecular properties that depend strongly on the electron correlation or reflect a breakdown in the single-configuration model, such as bond energies and the detailed shapes of potential energy surfaces. With some modifications and restrictions it also allows the

calculation of the energy separation of electronic states. As an example we showed in some detail how the method works for the Li_2 molecule, which is small enough that a parallel all-electron calculation is feasible. The results of the two calculations in terms of valence orbitals and dissociation energies were found to be in excellent agreement. A copy of this paper is included below in Appendix B.

B. NOCOR Studies of Representative Systems

At the same time we were extending the theoretical basis of our computational procedure, we continued to apply our existing programs to molecular systems that exhibit unusual and/or theoretically important types of chemical bonding. For example we have studied the structure of the polyiodide ions[3], I_3^- and I_5^-. These have a polymeric structure that is not manifested by similar chemical elements. In a crystal lattice, they are known to have an unusual zigzag shape with sets of three I atoms being colinear. We calculated the detailed electronic and geometrical structure of these ions. In addition we performed an extensive study of the way in which the presence and symmetry of the crystal lattice can influence the ionic geometry. We found the remarkable result that in the I_n^- compounds the charge alternates between even- and odd-numbered atoms in a regular fashion. In addition the bending force constants also exhibit a very marked alternation, with every second bond angle being stiff, and alternate angles having a force constant close to zero allowing the angle to vary freely. Thus *in vacuo* or in a symmetric crystal lattice, these chains would be linear. However in a lattice that is even slightly asymmetric, the chains are bent in the experimentally observed pattern. This is apparently a type a chemical behavior that had not been observed before.

The next molecule of this series that we studied was the organometallic compound cyclopentadienylthallium(I)[4]. The structure of this molecule is a "half-sandwich" with the bond from the metal to the cyclopentadiene ring being symmetric about the center of the ring. This type of bonding in a heavy element such as thallium had not been theoretically studied before. We performed a detailed analysis of its electronic structure to determine the exact nature of the bonding. We found that about one half of the bonding is electrostatic interaction between a Tl^+ and $C_5H_5^-$ ion. The covalent bonding was found to be primarily of π symmetry, as might be expected. Further, although the neutral Tl atom has an electronic configuration s^2p, which is not favorable for such

bonding, in the molecule almost a full electron charge (0.69 e) is promoted to contracted outer d orbitals. This strongly favors π bonding. Specifically most of the metal-ring bonding results from a valence orbital of e_1 symmetry in which the thallium atom has pd^2 hybridization. This hybridization is significant in that it is a "directed π bond", that is, of an e symmetry but strongly polarized in one direction. From this observation it was possible to explain the structure of not only this compound, but many chemically related ones. Thus the metal-ring bond is weaker in C_5H_5In, which lacks available valence d orbitals. The elements Au and Hg lack the valence p electron and hence cannot form the type of bond we observed in the Tl compound. This explains why these elements form σ rather than π complexes. Thus our calculation was able to correlate much of the experimental data on these systems.

The next three papers of this series were done in collaboration with Mr. Michael Rothman, a graduate student from the University of Michigan, Ann Arbor, who came to this site to learn the NOCOR method. After returning to that campus he, along with Professors Lawrence Bartell and Lawrence Lohr, began a productive research program independent from ours, using our computer programs to study unusual inorganic systems. We describe here only the work in which we were directly involved.

The first study we proposed in this series dealt with the Te_4^{2+} ion[5]. This is an unusual system in several respects: it is an inorganic aromatic ring structure that satisfies the 4n+2 rule, and has a Hückel bond order of 1.5. It was one of the first Te compounds to be discovered, is extremely stable in solution, and displays a remarkable bright red color. We undertook a detailed study of its geometric and electronic structure, with and without the presence of oppositely-charged counterions. We obtained a bond length *in vacuo* of 2.6108Å, and 2.6739Å with counterions. The latter compares well with the experimental bond length in crystals of 2.6633 - 2.6738Å. The molecular structure was found to be square and planar, as expected. We were also able to calculate the electronic transition that accounts for the color. This was the first practical application of our new effective-potential MCSCF program. Although it had been the object of much debate previously, we were able to show that this transition is $\pi \rightarrow \pi^*$ and we were also able to assign another experimentally observed transition as $n \rightarrow \pi^*$. Finally we calculated all of the (five) vibration frequencies. Four of these had been assigned experimentally. We were able to prove that two of the four vibrational bands had previously been misassigned due to being masked by stronger lines in the experimental spectrum.

The final two papers of this series concerned the properties of the hypervalent xenon fluorides. The first paper[6] studied the structures and detailed intramolecular potential energy surface of XeF_2 and XeF_4. Although these compounds are of some interest in their own right, we also felt it to be desirable to perfect the basis set and other aspects of the computation before attacking the more highly fluorinated compounds. A minimal basis set was developed that is considerably more accurate for this type of calculation than the usual atom-optimized set. The calculation reproduced the correct symmetries of both compounds. The bond lengths that resulted were somewhat too long, but gave the correct difference between the two molecules. Also, although the stretching force constants were slightly too large, the interaction force constants were found to be in good agreement with experiment, as was the anharmonicity. This was the first time that such a detailed analysis of the vibrational potential of such a relatively large molecule had been carried out. We felt it reflected sufficient accuracy to warrant the study of the two additional xenon fluorides, whose structures are of considerably more theoretical and experimental interest.

These two systems, which were the subject of the subsequent paper[7], are XeF_5^+ and XeF_6. Both of these are of considerable theoretical and experimental interest, since they have long been known to exhibit a number of puzzeling thermodynamic and spectroscopic properties. The structures of both species are governed by a stereochemically-active lone pair of electrons. We undertook a very detailed study of the structures of both species and also their force fields, including quadratic, cubic and quartic terms. The structure we obtained for XeF_5^+ was found to be in excellent agreement with experiment. For example the angle between bonds to the axial and equitorial F atoms was calculated to be 80.8^0, in comparison to the experimental value of 79.0^0. However the major question has long been the structure of XeF_6. It is known, from electron-diffraction data, to be nonrigid and possess a C_{3v} symmetry that is slightly deformed from an octahedron. Our calculations bore this out, showing the structure of lowest energy to be of this symmetry. Plotting the electron density in the molecular orbitals, we were able to show graphically the presence and position of the lone electron pair. This protrudes through one of the triangular faces if the structure is constrained to be octahedral, and hence causes its distortion. The final structure we obtained is in good agreement with electron diffraction results: the angle between the C_{3v} axis and an F atom in the opened

face was 79.4^0, which may be compared to the experimental value of 67.5^0. The angle between the C_{3v} axis and an F in the opposite face was 47.4^0 in comparison the the experimental value 52.3^0. However the barrier to hindered pseudorotation, that is the energy to move the electron pair between different faces of the molecule, was somewhat too high to explain the rapid interconversion of conformations that is observed experimentally at room temperature. This reflects the fact, shown by the above distortion angles, that our calculated structure was slightly too distorted. Nonetheless, our calculations ended a long controversy by confirming the structure indicated by spectroscopic data and demonstrating its electronic origins. Finally, in comparing XeF_6 and XeF_5^+ with the other two xenon compounds, it was found that the trends in their respective orbital energies and equilibrium bond lengths were well described by our calculations.

C. Ab Initio Vibrational Spectra

As an outgrowth of our work on unusual types of bonding and their confirmation by computed spectroscopic properties, we calculated the infrared and Raman spectra of the thiirene molecule[8], C_2H_2S. This project was carried out in collaboration with Professors Schaad and Hess of this department. Thiirene is a ring compound, which due to its strongly antiaromatic electronic structure is unstable and may be studied only by its spectra in matrices at low temperature. These types of spectra invariably contain lines from many other species. Thus it is extremely useful to calculate those parts of the spectrum which correspond to a particular species in order to confirm its structure. For this work we employed an all-electron SCF calculation using a moderately large (4-31G) basis. We computed all the vibrational bands of both C_2H_2S and C_2D_2S, including both their frequency and, in the case of infrared bands, their relative intensities. Our computed structure exhibited an unusually long C-S bond and a fairly short (1.2509Å) C=C bond, as might be expected from the system's antiaromatic electronic structure. We were able to reproduce all the lines of the experimental spectra in each species except for a pair of lines in each, which we showed had been experimentally misassigned. The spectroscopists subsequently reevaluated the spectra and brought the assignments into accord with our calculations. The final result of this work was to confirm the postulated structure of this species.

D. Mechanism of the H_2 Exchange Reaction

During our work with MCSCF calculations on small molecules, we became interested in the $H_2 + D_2$ exchange reaction[9]. This system is important from a theoretical viewpoint as the prototype for all four-center reactions and also of the energy surfaces of reacting diatomic molecules in general. However for a number of years this reaction has completely defied all theoretical explanation, since the experimental evidence indicates a four–center transition state with an activiation energy much less than any that has been calculated from first principles. In collaboration with Michael Rothman and Lawrence Lohr of the University of Michigan, Ann Arbor, we began a series of calculations of interacting H_2 molecules using a large basis set and a set of 20 optimized configurations in an MCSCF calculation. We developed a technique for studying this type of system by which the centers of mass of the interacting molecules are gradually brought together, all other degrees of freedom being simultaneously optimized to provide the minimum energy. Along this path we then searched for the transition state, defined as the point at which the energy could decrease along one of these other degrees of freedom, thus dissociating into products. In this way we located an energy which is a lower bound to the transition state energy. Our value, 193 kJ mol^{-1} is 34 kJ mol^{-1} above the experimental activation energy. Hence we were able to demonstrate that, at least to this level of accuracy, the experimental measurements are inconsistent with a bimolecular mechanism.

E. Computation of Core Energy Levels in Atoms and Small Molecules

As an outgrowth of our work on core-valence partitioning and relativistic effects, we began a very productive collaboration with M. S. Banna of this department, who works in the area of X-ray photoelectron spectra (XPS) of atoms and small molecules. This type of spectroscopy employs a monochromatic beam of X-rays to ionize core electrons, measuring the minimum energy required for the ionization to take place. The XPS spectra of free atoms pose, except for the inert gases, a difficult experimental problem, but one that is central to understanding the interaction of high-energy radiation with matter. It is also useful in studying the nature of bonding in solid materials. We realized that our computer programs might be very useful in predicting and interpreting the XPS spectra in two cases: small molecules composed of

light atoms, for which relativistic effects are small; and heavy atoms, for which the relativistic effects are comparatively well-understood. Surprisingly good accuracy was found for the core ionization energies we calculated in both types of systems. This has been the basis of three papers so far.

In the first paper[10], Dr. Banna reported for the first time the X-ray spectrum of an alkali halide in the gas phase, CsI. To check and interpret his results, and also to test our computational procedure, we carried out relativistic (Dirac-Fock) calculations of the observed $3d_{5/2}$ ionization in Cs, I, and their singly-charged ions. Using these results in conjunction with the experimental energies, it was possible to analyze the nature of the bonding of the CsI molecule in terms of covalent and ionic contributions. We also studied the ionization process in terms of atomic and extraatomic relaxation energies, which also reflect the charge distribution of the neutral molecule. One of the most useful results of this work was the discovery that the relativistic atomic structure program gave very precise estimates of core binding energies for experimentally known transitions. They were also appreciably more accurate than the best theoretical values previously available. For example, the best previous value for the ionization of the Cs atom was 749.7eV. We calculated 732.1, while the experimental value is 731.8. Likewise for the I atom, the best previous value was 643.0eV. We calculated 627.9, while the experiment gives 628.1. The linewidth of the X-ray line is typically 0.1eV. Therefore we concluded that our method is sufficiently accurate that it may be used to calculate ionization in that great majority of atomic systems that can not be studied experimentally, and these results may be reliably used to interpret experimental results for molecules.

Our second paper[11] dealt with the use of nonrelativistic molecular SCF programs to study the ionization of small molecules composed of light elements. We compared the compounds ozone, O_3, and oxygen difluoride, OF_2. These have long been an enigma in the understanding of the electronic structures of these types of molecules, because the ionization of the central O atom of ozone is of very high energy compared to other oxygen compounds, indicating a large positive charge on that atom. It is higher than the oxygen of OF_2, even though F is a much more electronegative element. We calculated all four of the core ionization energies, using a large (4s3p) gaussian basis set and finding the energies of the open-shell hole states using the BISONMC MCSCF program. First we showed that the calculation gives good agreement with experiment, except for the central O of ozone. However all the experimentally observed

trends were reproduced. The error for the central O of ozone was 1.68eV. For comparison, the error for the terminal O was 0.04eV. In OF_2 the error for the O atom was 0.23 and for the F atoms, 0.44. In terms of relative accuracy, these final three values are in error by approximately 0.05% . We calculated the central oxygen of ozone to possess an ionization 2.45eV higher than in OF_2; the experimental value is 1.0eV. This difference is probably due to our neglect of d orbitals in the basis set for ozone, since these are known to to affect the central atom most strongly. We then carried out a population analysis of the electronic structures of both compounds. This showed that although the F atom withdraws considerable charge from the O atoms in OF_2, it does so only through the σ orbitals. The transfer is small through the π orbitals even though the π overlap is large. The transfer of charge is small in the σ orbitals of ozone, but very large and in the opposite direction in the π orbitals. Approximately 0.2 electron is shifted from the central oxygen in this way. Thus the XPS spectra essentially reflect the π bonding present in ozone but not in OF_2.

In our third paper[12], we carried out a series of comparisons of the atomic core electron ionization energies of several atoms and atomic ions. The choice of the particular elements and orbitals chosen was dictated by the availability of experimental data. We compared Hartree-Fock, Dirac-Slater, and our Dirac-Fock approaches. In this case we also included J-dependent terms, thus obtaining all four possible transitions that would correspond to a spin-orbit pair or a single Hartree-Fock orbital. Our results were found to be more accurate than any that have been previously reported, and this agreement is seen to be largely independent of atomic number or valence electron configuration. This paper is included below as Appendix C.

Properties of the X State of Pb_2

	E_v(eV)	R_e(Å)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})
nonrelativistic SCF	-161.58	2.985	172.2	0.217
nonrelativistic MCSCF	-164.52	3.178	133.3	0.008
relativistic SCF	-227.78	2.679	204.3	0.287
relativistic MCSCF	-229.37	2.836	137.8	0.272
experiment*	-	?	109.8	0.269

*V.E. Bondybey and J.H. English, *J.Chem.Phys.* 67, 3405 (1977)

III. Summary of New Theories and Computer Programs

A. Comparison of Effective Potential Methods of Varying Levels of Accuracy

As noted at the beginning of this report, our original NOCOR method for carrying out valence-only molecular calculations was straightforward to apply to any system and gave quite accurate results, but was limited to nonrelativistic single-configuration calculations. Now we have removed these restrictions. So it is of interest to examine how their presence or absence affects molecular properties. We therefore undertook a study of the spectroscopic properties of a quite heavy diatomic compound, Pb_2. To obtain reasonable accuracy, we first needed to generate a basis set, since the standard tables do not extend this far down the Periodic Table. We therefore carried out a number of atomic calculations to optimize a complete double-zeta basis for the Pb atom. The valence part (6s,6p) is then suitable for forming molecular orbitals. We then performed nonrelativistic SCF and six-configuration MCSCF calculations to determine the total valence energy E_v, equilibrium bond length R_e, first vibrational frequency ω_e and anharmonicity $\omega_e x_e$. We then calculated these same properties by both the SCF and MCSCF methods but employing relativistic (Dirac-Fock) core orbitals. The results are shown and compared with the available experimental data in Table I. The experimental R_e is not known, but is thought to be about 2.9 Å. From this table it may be seen that the relativistic valence energies are much lower than the nonrelativistic ones, reflecting the strong contraction of the s and p core orbitals in the former case. SCF bond lengths are always shorter and vibrational frequencies higher than in the more accurate MCSCF results, since SCF wavefunctions must dissociate to spurious excited electronic states at infinite bond length. Also relativistic calculations are always more tightly bound, with shorter bond lengths and higher vibrational frequencies due to the contraction of the core orbitals. The effect of correlation energy, present in the MCSCF results, is about as large as those due to relativity. But the final results, embodying both effects, are the most accurate. Any calculation that employed one but not the other of these effects would have implied an incorrect conclusion as to which terms are important in determining the nature of the bonding. This work is currently being prepared for publication.

B. Full Dirac-Fock Theory of Molecules

In order to incorporate relativistic effects rigorously into effective potential calculations, it is first necessary to first develop a method for determining the exect four-component (Dirac-Fock) orbitals for molecules. This had not heretofore been achieved, due to computational complexity. In our previous work we had employed only relativistic core orbitals, thus avoiding the calculation of multicenter terms with these types of orbitals. However it is clearly desirable to treat the valence on this level also, since it would allow the use of j–j coupling and hence such important properties as spin-orbit splitting in molecules. We have now, in collaboration with Prof. S. N. Datta who was a postdoctoral associate with our group, developed a complete new computer program which achieves this result. This program solves the Dirac-Fock equations for both atoms and molecules using a basis set of gaussian functions, which are appropriate for computing multi-center integrals.

It is interesting that in the Dirac theory, the total energy of an atom or molecule is unstable in a variational calculation with respect to the formation of antiparticles, in this case a positrons, with the decrease in energy of $2mc^2$. This is very similar to the variational collapse that occurs in valence-only calculations when the pseudopotential is not present. Datta was able to prove that our effective potential (NOCOR) formalism could be applied directly to the case of variational collapse in the Dirac equation[13]. This is the only method derived thus far which permits Dirac-Fock calculations on molecules without the variational collapse to $-2mc^2$, and has been included in our program.

In determining appropriate basis sets, it was soon discovered that entirely different procedures were required from the nonrelativistic case. For example the imaginary terms proved much more difficult to expand than the real ones. Also, due to the presence of two coupled radial components, increasing the number of basis functions did not always give a more precise result. This problem was solved by constraining the basis always exactly to reproduce the correct one-electron terms in the relativistic energy. It was found that ten-term gaussian basis sets gave a good estimate of the relativistic correction to the energy and were sufficiently compact for molecular calculations. For example, using this procedure to generate a basis for the Be atom, we found a total energy of -14.574078 hartrees. The analogous nonrelativistic value is -14.572579. The exact relativistic value found using numerical methods is -14.575189. Since the known relativistic energy correction is .00217, it is seen that our simple ten-term basis has given 69% of this effect. We have calculated the Be_2 molecule in

the same way and found essentially the same qualitative result. Of course Be_2 is too light to have a measurable shift in its binding energy, *i.e.* the difference between the molecule and its constituate atoms.

Our first paper describing this work is nearly finished. We hope in the near future to extend our calculations to heavier systems. The program in essentially its present form may be used in effective-potential calculations as well, where the effects we have studied will be much more pronounced.

C. Symmetries of Transition States in Isoenergetic Reactions

Finally, one additional finding developed from our work on the diatomic exchange reaction described earlier. This was a study of the symmetries of these reactions in terms of their nuclear geometries. In the absence of a detailed knowledge of the precise geometry of the transition state of a reaction, one may study the activation energy of a reaction in two ways: either by bringing the centers of mass of two interacting molcules together along the minimal-energy pathway, or by choosing the minimal symmetry the transition state must have, and then minimising the energy of this structure. In the paper described above, we took the first approach. But in the course of this work, we also developed the second, which may be at least as useful.

This approach is restricted to the special case of isoenergetic reactions, *i.e.* those in which products and reactants have the same total energy. In this case we were able to prove that the transition state must have at least one element of symmetry. Further we proposed the concept of "symmetrically equivalent groups", and using these worked out the symmetries of transition states for any three- and four-center reaction. In particular we proved that for any four-center mechanism involving diatomic molecules, the transition state must be of C_{2v} symmetry with a perpendicular symmetry plane passing through two, and only two, of the atoms. Thus in determining the transition state energy of reacting diatomics by *ab initio* computations, one need only optimize the energy of a structure of this symmetry.

Since this work is not closely related to any of the others, it is included below as Appendix D.

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APPLICATION OF EFFECTIVE POTENTIALS TO RELATIVISTIC HARTREE–FOCK CALCULATIONS

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The Phillips–Kleinman pseudopotential and the operator equivalence techniques for calculating effective potentials are applied directly to the Dirac–Hartree–Fock calculation of molecular properties. The results based on both relativistic and nonrelativistic core functions are compared for the PbO molecule.

1. Introduction

The recent development of effective-potential theory has allowed accurate calculations to be performed on the structure and properties of molecules composed of elements from all regions of the periodic table. It has been suggested [1] that relativistic effects might be significant in compounds of fifth-row and heavier elements, such as Pb. Since the advantages of effective-potential theory in quantum-chemical calculations should be most pronounced for compounds of such heavy elements, it would be especially valuable to be able to include these relativistic contributions in the core potential.

As part of our ongoing investigations of molecular quantum calculations involving heavy atoms, we conceived about two years ago the approach described in this paper. This treatment is based on the assumption that only the core orbitals are inherently relativistic, and hence relativistic effects on the valence orbitals are indirect, through core–valence electron–electron interactions. In this paper we develop a valence-electron theory based on the Dirac–Fock hamiltonian, specifically defining the relativistic Phillips–Kleinman operator, as well as calculating the corresponding local Coulomb and exchange potential functions. Finally we apply our theory to some properties of the PbO molecule and compare our results with the analogous nonrelativistic results, with experiment and with a nonrelativistic all-electron calculation [2].

2. Valence-electron treatment of the Dirac–Hartree–Fock theory

The relativistic hamiltonian for a many-electron system may be written as [3]

$$H^0 = \sum_{\mu} H_D(\mu) + \sum_{\mu>\nu} r_{\mu,\nu}^{-1} + V_{nn} , \tag{1}$$

where V_{nn} is the nuclear–nuclear repulsion term, if any, and $H_D(\mu)$ is the standard Dirac one-electron hamiltonian in the field of nuclear potential V,

$$H_D(\mu) = \alpha_\mu \cdot p_\mu c + \beta_\mu c^2 + V_\mu , \quad V_\mu = -\sum_{p}^{\text{nuclei}} Z_p / r_{\mu p} . \tag{2}$$

The terms in eq. (2) retain their usual meaning [3]. In this paper we will not consider Breit interactions or any

other higher-order relativistic corrections, so that the total energy may be written as the expectation value of H^0

$$E^0 = \langle H^0 \rangle = \sum_a I_a + \tfrac{1}{2} \sum_{a,b} (J_{ab} - K_{ab}) + V_{nn} , \tag{3}$$

where

$$I_a = \langle \psi_a | H_D | \psi_a \rangle , \quad J_{ab} = \langle \psi_a(1)\psi_b(2) | r_{12}^{-1} | \psi_a(1)\psi_b(2) \rangle , \quad K_{ab} = \langle \psi_a(1)\psi_b(2) | r_{12}^{-1} | \psi_a(2)\psi_b(1) \rangle .$$

If we assume that the orbitals of the system may be divided into strongly-orthogonal core and valence sets [4], minimization of $\langle H^0 \rangle$ is equivalent to the minimization of $E_v^0 + \tilde{V}_{nn}$ where $\tilde{V}_{nn}$ is the screened nuclear–nuclear repulsion and E_v^0 is given by

$$E_v^0 = \langle \Psi_v | \hat{H}_v^0 | \Psi_v \rangle , \tag{4}$$

where

$$\hat{H}_v^0 = \sum_{\mu}^{N_v} H_D'(\mu) + \tfrac{1}{2} \sum_{\mu \neq \nu}^{N_v N_v} r_{\mu,\nu}^{-1} , \quad H_D'(\mu) = H_D(\mu) + \sum_{p}^{\text{nuclei}} \sum_{j=1}^{N_{cp}} (J_{cp}^j - K_{cp}^j) .$$

J_{cp}^j and K_{cp}^j are the conventional direct and exchange operators involving the jth core orbital of the pth atom, all core orbitals being held constant.

The atomic orbitals that minimize the value of an atomic $\langle H^0 \rangle$ are characterized in general by the quantum numbers

$$n = n_r + |\kappa| , \quad j = -(\kappa a + \tfrac{1}{2}) , \quad m = -j, -j+1, \ldots, j \quad \text{and} \quad a = \pm 1$$

as discussed elsewhere [3] and can be written in terms of the two-component angular functions $\chi_{\pm\kappa,m}(\theta, \phi)$ as

$$\psi_{n\kappa m}(r, \theta, \phi) = r^{-1} \begin{pmatrix} P_{n\kappa}(r) & \chi_{\kappa m}(\theta, \phi) \\ iQ_{n\kappa}(r) & \chi_{-\kappa m}(\theta, \phi) \end{pmatrix} , \tag{5}$$

where the radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are conventionally called the "large" and "small" components. The orthonormality conditions of the atomic orbitals are given by (after using the symmetry properties of $\chi_{\kappa m}$)

$$\int_0^{\infty} dr (P_a P_b + Q_a Q_b) = \delta_{n_a n_b} \delta_{l_a l_b} \delta_{a_a a_b} . \tag{6}$$

Next we consider the valence-electron problem for an atomic case in terms of these functions. The atomic core is assumed to consist of a set of relativistically closed groups $\mathcal{A}$, each with the electronic population $q_{\mathcal{A}} = 2j_{\mathcal{A}} + 1$. Following the treatment of previous authors [3] one can show that for atoms, by analogy with the all-electron case,

$$E_v^0 = \sum_{\alpha=1}^{N_v} I_\alpha' + \tfrac{1}{2} \sum_{\alpha \neq \beta}^{N_v N_v} \sum_k [A^k(\alpha, \beta) F_k(\alpha, \beta) - B^k(\alpha, \beta) G_k(\alpha, \beta)] ,$$

$$I_\alpha' = I_\alpha + \sum_{\mathcal{A}} \left[F_0(\mathcal{A}, \alpha) - \tfrac{1}{2} \sum_k \Gamma_{l_{\mathcal{A}}\, k l_\alpha} G_k(\mathcal{A}, \alpha) \right] , \tag{7}$$

$$I_\alpha = \int_0^{\infty} dr \{ P_\alpha [c(dQ_\alpha/dr - \kappa_\alpha Q_\alpha/r) + (c^2 - V) P_\alpha] - Q_\alpha [c(dP_\alpha/dr + \kappa_\alpha P_\alpha/r) + (c^2 + V) Q_\alpha] \} ,$$

where A^k, B^k and $\Gamma_{l_{\mathcal{A}}\, k l_\alpha}$ are constant coefficients as defined by previous authors. The integrals $F_k(a, b)$ and $G_k(a, b)$ are given by

$$F_k(a,b) = \int_0^\infty [P_a^2(r) + Q_a^2(r)] r^{-1} Y_k(b,b;r)\,dr\,,$$

$$G_k(a,b) = \int_0^\infty [P_a(r)P_b(r) + Q_a(r)Q_b(r)] r^{-1} Y_k(a,b;r)\,dr\,, \tag{8}$$

$$Y_k(a,b;r) = r \int_0^\infty (r_<^k / r_>^{k+1}) [P_a(s)P_b(s) + Q_a(s)Q_b(s)]\,ds\,.$$

$r_<$ and $r_>$ are defined as the lesser and greater respectively of r and s. The variational problem, therefore, corresponds to the minimization of E_v^0 as given in eq. (7) subject to the orthonormality constraint (6). Thus the variational condition is of the general form

$$\Delta E_v^0 = \sum_{\alpha\beta} \epsilon_{\alpha\beta} \Delta \left[\int_0^\infty (P_\alpha P_\beta + Q_\alpha Q_\beta)\,dr \right]. \tag{9}$$

One may apply a unitary transformation to the radial components of both P_α and Q_α such that the lagrangian multipliers $\epsilon_{\alpha\beta}$ are brought into diagonal form $\epsilon_{\alpha\beta} \to \epsilon_{\alpha\beta} \delta_{n_\alpha, n_\beta} \delta_{k_\alpha, j_\beta} \delta_{a_\alpha, a_\beta}$. The resulting pseudoeigenvalue equation is written in the matrix form as

$$F \begin{pmatrix} P_\alpha \\ Q_\alpha \end{pmatrix} = \epsilon_{\alpha\alpha} \begin{pmatrix} P_\alpha \\ Q_\alpha \end{pmatrix}, \tag{10}$$

where the four elements of the F matrix are given by

$$F_{11} = (c^2 - V) + \sum_{\mathscr{A}} \left[r^{-1} Y_0(\mathscr{A}, \mathscr{A}; r) - \tfrac{1}{2} \sum_k \Gamma_{j_{\mathscr{A}}\ k l_\alpha} r^{-1} \Omega_{k\mathscr{A}}(r) \right]$$

$$+ \sum_\beta{}' \sum_k [A^k(\alpha,\beta) r^{-1} Y_k(\beta,\beta;r) - B^k(\alpha,\beta) r^{-1} \Omega_{k\beta}(r)]\,,$$

$$F_{12} = c(\mathrm{d}/\mathrm{d}r - \kappa/r), \quad F_{21} = -c(\mathrm{d}/\mathrm{d}r + \kappa/r)\,,$$

$$F_{22} = -(c^2 + V) + \sum_{\mathscr{A}} \left[r^{-1} Y_0(\mathscr{A}, \mathscr{A}; r) - \tfrac{1}{2} \sum_k \Gamma_{j_{\mathscr{A}}\ k l_\alpha} r^{-1} \Omega_{k\mathscr{A}}(r) \right]$$

$$+ \sum_\beta{}' \sum_k [A^k(\alpha,\beta) r^{-1} Y_k(\beta,\beta;r) - B^k(\alpha,\beta) r^{-1} \Omega_{k\beta}(r)]\,.$$

The primed summations are over all functions except α. The operator $\Omega_{k\gamma}$ is defined by

$$\Omega_{k\gamma} \begin{pmatrix} P_\alpha \\ Q_\alpha \end{pmatrix} \equiv \begin{pmatrix} P_\gamma \\ Q_\gamma \end{pmatrix} Y_k(\gamma, \alpha; r)\,. \tag{11}$$

After a little manipulation one obtains the familiar form of the valence-electronic energy

$$E_v^0 = \sum_{\alpha=1}^{N_v} (I'_\alpha + \epsilon_{\alpha\alpha})\,, \tag{12}$$

where $\varepsilon_\alpha = \epsilon_{\alpha\alpha}$ can be considered as the analogous orbital energy.

3. Relativistic Phillips–Kleinman pseudopotential and atomic local potential

Since eq. (10) is of the same form as that which occurs in the nonrelativistic case, we define the one-electron form of the atomic Phillips–Kleinman pseudopotential [5], after integrating over the angular coordinates,

$$V_\alpha^{PP} = \sum_\mu \left|\begin{pmatrix} P_A \\ Q_A \end{pmatrix}\right)(\varepsilon_\alpha - \varepsilon_\mu)\left(\left(P_\mu \; Q_\mu\right)\right| \times \text{angular terms} . \tag{13}$$

The pseudoeigenvalue equation (10) now reduces to

$$(F + V_\alpha^{PP})\begin{pmatrix} \tilde{P}_\alpha \\ \tilde{Q}_\alpha \end{pmatrix} = \varepsilon_\alpha \begin{pmatrix} \tilde{P}_\alpha \\ \tilde{Q}_\alpha \end{pmatrix}, \tag{14}$$

where $\tilde{P}_\alpha$ and $\tilde{Q}_\alpha$ are the radial components of the αth valence pseudowavefunction.

In order to calculate the relativistic analogue of the atomic local potential [6], we define a new formal Fock matrix $\hat{F}$ in the space spanned by the pseudowavefunctions as

$$\hat{F}_{11} = \sum_\beta{}' \sum_k \left[A^k(\alpha,\beta) r^{-1} \hat{Y}_k(\beta,\beta;r) - B^k(\alpha,\beta) r^{-1} \hat{\Omega}_{k\beta}(r)\right] + (c^2 - V) ,$$

$$\hat{F}_{12} = F_{12}, \quad \hat{F}_{21} = F_{21} , \tag{15}$$

$$\hat{F}_{22} = \sum_\beta{}' \sum_k \left[A^k(\alpha,\beta) r^{-1} \hat{Y}_k(\beta,\beta;r) - B^k(\alpha,\beta) r^{-1} \hat{\Omega}_{k\beta}(r)\right] - (c^2 + V) ,$$

where

$$\hat{Y}_k(\beta,\beta;r)\begin{Bmatrix} \tilde{P}_\alpha(r) \\ \tilde{Q}_\alpha(r) \end{Bmatrix} \equiv \begin{Bmatrix} \tilde{P}_\alpha(r) \\ \tilde{Q}_\alpha(r) \end{Bmatrix} r \int_0^\infty (r_<^k / r_>^{k+1})[\tilde{P}_\beta^2(s) + \tilde{Q}_\beta^2(s)]\,ds$$

and

$$\hat{\Omega}_{k\beta}(r)\begin{Bmatrix} \tilde{P}_\alpha(r) \\ \tilde{Q}_\alpha(r) \end{Bmatrix} \equiv \begin{Bmatrix} \tilde{P}_\beta(r) \\ \tilde{Q}_\beta(r) \end{Bmatrix} r \int_0^\infty (r_<^k / r_>^{k+1})[\tilde{P}_\alpha(s)\tilde{P}_\beta(s) + \tilde{Q}_\alpha(s)\tilde{Q}_\beta(s)]\,ds .$$

Eq. (14) is now equivalent to

$$(\hat{F} + V^{PP} + W^\alpha)\begin{pmatrix} \tilde{P}_\alpha \\ \tilde{Q}_\alpha \end{pmatrix} = \varepsilon_\alpha \begin{pmatrix} \tilde{P}_\alpha \\ \tilde{Q}_\alpha \end{pmatrix}, \tag{16}$$

where W^α is an atomic local potential matrix, and $V^{PP} + W^\alpha \equiv V^{eff}$ is the effective potential matrix for the valence-electron treatment. Comparing eqs. (14) and (16) one can write from the operator equivalence condition [6]

$$W^\alpha \begin{pmatrix} \tilde{P}_\alpha \\ \tilde{Q}_\alpha \end{pmatrix} = (F - \hat{F})\begin{pmatrix} \tilde{P}_\alpha \\ \tilde{Q}_\alpha \end{pmatrix}, \tag{17}$$

whereby W^α can be explicitly written as

$$W^{\alpha} = \begin{pmatrix} W_{11} & 0 \\ 0 & W_{22} \end{pmatrix} \tag{18}$$

$$W^{\alpha}_{11,22} = W^{c\alpha}_{11,22} + W^{v\alpha}_{11,22} ,$$

$$W^{c\alpha}_{11,22} = \sum_{\mathscr{A}} q_{\mathscr{A}} \left[r^{-1} Y_0(\mathscr{A}, \mathscr{A}; r) - \tfrac{1}{2} \sum_k \Gamma_{j_{\mathscr{A}}\, k j_\alpha} r^{-1} \Omega_{k\mathscr{A}}(r) \right] \tilde{P}_\alpha, \tilde{Q}_\alpha / \tilde{P}_\alpha, \tilde{Q}_\alpha ,$$

$$W^{v\alpha}_{11,22} = \sum_{\beta}{}' \sum_k \{ A^k(\alpha,\beta) r^{-1} [Y_k(\beta,\beta;r) - \hat{Y}_k(\beta,\beta;r)]$$

$$- B^k(\alpha,\beta) r^{-1} [\Omega_{k\beta}(r) - \hat{\Omega}_{k\beta}(r)] \} \tilde{P}_\alpha, \tilde{Q}_\alpha / \tilde{P}_\alpha, \tilde{Q}_\alpha .$$

Thus after determining the effective potential one may then solve the pseudoeigenvalue equation (16) for an atom and, assuming the W^{α} are transferable, for a molecule [6].

4. Nonrelativistic limit for the valence electrons

Since the magnitude of the relativistic one-electron effect depends on the shielded nuclear charge for any orbital, it is reasonable to believe that the valence-electronic behaviour is approximately nonrelativistic except through the indirect effect of interaction with the core electrons for whom the relativistic effect is predominant. Eq. (10) is equivalent to a set of coupled equations

$$F_{11} P_\alpha + F_{12} Q_\alpha = \varepsilon_\alpha P_\alpha , \quad F_{21} Q_\alpha + F_{22} P_\alpha = \varepsilon_\alpha Q_\alpha .$$

Recognizing $\varepsilon_\alpha = c^2 + \varepsilon'_\alpha$ and neglecting the terms independent of c in the second coupled equation gives the familiar nonrelativistic limit as $v/c \to 0$, where v is the electron velocity. A contraction of the modified Fock matrix in the subspace spanned by the "large" components gives the pseudoeigenvalue equation

$$\bar{F} P_\alpha \equiv \Big\{ -(d^2/dr^2) + \kappa_\alpha(\kappa_\alpha + 1)/2r^2 + \sum_{\mathscr{A}} q_{\mathscr{A}} \left[r^{-1} Y_0(\mathscr{A}, \mathscr{A}; r) - \tfrac{1}{2} \sum_k \Gamma_{j_{\mathscr{A}}\, k j_\alpha} r^{-1} \Omega_{k\mathscr{A}}(r) \right]$$

$$+ \sum_{\beta}{}' \sum_k [A^k(\alpha,\beta) r^{-1} Y_k(\beta,\beta;r) - B^k(\alpha,\beta) r^{-1} \Omega_{k\beta}(r)] \Big\} P_\alpha(r) = \varepsilon'_\alpha P_\alpha(r) . \tag{19}$$

ε'_α is the analogue of the nonrelativistic valence-orbital energy, where the core has been described relativistically. The contracted effective potential W^{con} is equal to W_{11} since W_{22} has been neglected in comparison to c.

A further simplification arises by noting that as $c \to \infty$, $Q \to 0$. In the limit $Q = 0$ we will denote the corresponding quantities with a prime. In that case the orthogonality condition is given by

$$\int_0^\infty P_{\mathscr{A}}(r) P'_\alpha(r) \, dr = 0, \quad \int_0^\infty P'_\alpha(r) P'_\beta(r) \, dr = \delta_{n_\alpha, n_\beta} \delta_{l_\alpha, l_\beta} \delta_{\sigma_\alpha, \sigma_\beta} . \tag{20}$$

With this choice of the large components the Phillips-Kleinman pseudopotential is strictly determined from only the large components of the core. The atomic local potential is also considerably simplified and is defined only for the large component of a pseudovalence-function. This is then identical with W_{11} as defined by eq. (18) with the necessary modifications of the radial components, $P_\alpha \to P'_\alpha$, $Q_\alpha \to 0$. Thus in the expansion of W_{11} in eq. (18) all the Y and Ω integrals will be independent of any Q components in this case except the integral $Y_0(\mathscr{A}, \mathscr{A}; r)$, in which the core Q components still contribute. Therefore one may generate the effective potential for each of the

constituent atoms of a molecule and finally solve the molecular pseudoeigenvalue problem [6]. The molecular Fock operator so obtained is defined in the space spanned only by the valence pseudowavefunctions corresponding to the radial components $\tilde{P}'$ and is identical in form with its nonrelativistic analog.

5. Sample computations and discussion

As a test of this theory we have carried out parallel relativistic and nonrelativistic calculations for some properties of PbO. The relativistic atomic functions were obtained by the numerical Dirac-Fock procedure [7]. The valence basis functions and nonrelativistic core functions were taken from atomic double-zeta SCF calculations[‡]. The valence functions were defined to be the 6s and 6p orbitals of Pb and the 2s and 2p orbitals of O. The core potentials $W^{c\alpha}$ and the pseudopotentials were found by the method described above. The $W^{v\alpha}$ potential, due to valence–valence interactions, was generated from the nonrelativistic atomic orbitals and assumed to be the same in both cases. The W^{α} functions were found separately for each member of the basis set. For the O atom, only nonrelativistic functions were employed.

In table 1 we list the orbital energies, equilibrium bond lengths and vibrational frequencies obtained from these two calculations. We also compare the latter two properties, for which the SCF approximation usually gives accurate results, with the experimental values [9]. The orbital energies are seen to be considerably different in the two calculations, the relativistic values being lower, although the bond lengths and frequencies are nearly the same. As might be expected [1], the bond length in the relativistic case is slightly shorter.

In interpreting these results it should be pointed out that although most of the relativistic core orbitals of Pb are less diffuse than the analogous nonrelativistic ones, the relativistic 4f, 4f*, 5d and 5d* are slightly more diffuse. Therefore the relativistic contraction of the 5s, and 5p is largely offset by the 4f and 5d functions, particularly in the local potential. Qualitative predictions, such as the occurrence of shorter bond lengths in the relativistic case, based on the assumption that all relativistic core orbitals are more contracted, are not necessarily valid.

It is also useful to compare these results with those of Schwenzer et al. [2], who performed a unique minimal-basis set all-electron SCF calculation on PbO. These authors compared their results with experiment in order to estimate the magnitude of relativistic effects. It is interesting to note that our nonrelativistic results are in appreciably better agreement with experiment than theirs (1.871 Å for the bond length and 868 cm^{-1} for the frequency), indicating that most of their discrepancy with experiment was due to the limited basis set employed, rather than to use of the nonrelativistic hamiltonian.

We conclude that for the observable properties in table 1 the relativistic and nonrelativistic results are nearly the same. This is in agreement with the general conclusions of Schwenzer et al. but not with those of Desclaux and

[‡] The oxygen orbitals are from ref. [8]. The lead orbitals and basis were obtained from atom optimization. Details of the lead basis set will be published elsewhere.

Table 1
Computed properties of PbO

	Nonrelativistic	Relativistic	Experimental
orbital energies (au)			
$\epsilon_{15\sigma}$	−1.120	−1.274	–
$\epsilon_{16\sigma}$	−0.464	−0.878	–
$\epsilon_{17\sigma}$	−0.283	−0.418	–
$\epsilon_{9\pi}$	−0.396	−0.484	–
bond length (Å)	1.910	1.903	1.922
vibrational frequency (cm^{-1})	749	760	721

Pyykko [1], who found a much larger difference in PbH_4 using the spherical approximation. The results found by Das and Wahl [10] using a different valence-electron method suggest that relativistic effects may be much more important in properties such as electronic transition energies, rather than in ground-state properties.

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APPENDIX B.

On the Use of Pseudopotentials and Effective Potentials in Molecular MCSCF Calculations

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Abstract

A general theoretical approach and computational method are described for employing pseudopotential operators to simplify ab initio molecular multi-configuration SCF calculations. Considerable computational effort may be saved in this way since only the valence orbitals need be computed explicitly. Using the ground electronic state of Li_2 as an example, the role of the Lagrange multipliers that arise in the MCSCF formalism is discussed. The pseudopotential and effective potential approaches described herein are shown to accurately reproduce the detailed electronic structure, including configuration-mixing coefficients, of Li_2.

1. Introduction

In recent years there has been an increasing interest in techniques for carrying out ab initio studies of atomic and molecular properties treating only valence orbitals explicitly. Such techniques are greatly extend the number of chemical systems that are amenable to precise theoretical calculations. In particular they facilitate the study of molecules containing heavy elements, in which the numbers of core electrons is large. But in principle the valence-only approach allows most of the properties of any system, for a given amount of computational effort, to be found more precisely.

We have previously described a general theoretical approach that allows carrying out self-consistent-field calculations, treating only valence orbitals, that parallels conventional SCF methods, [1, 2] We now wish to extend our theoretical development to the more general cases of open-shell SCF and multiconfiguration SCF (MCSCF) applications. This extension is clearly necessary in order to predict important properties - for example, dissociation energies of inorganic compounds.

Other workers have reported successful valence molecular-orbital calculations using open-shell SCF and MCSCF methods.[3-6] These have all been based on what might be termed the core-potential approximation, i.e. that the effect of the core electron distribution on the valence may be represented by potential functions characteristic of the core but independent of the valence orbitals. This approximation simplifies calculations, but its accuracy and theoretical basis have not been studied.

In this paper we will show how one-electron Phillips-Kleinman pseudopotential operators, which replace core-valence orthogonality constraints in valence-only calculations, may be employed in MCSCF calculations. This derivation is nonempirical and follows from the variation condition imposed on the total energy. The sum of all terms that simulate the effect of

core orbitals on the valence we refer to as an effective potential to distinguish it from pseudopotentials (although the former contains nonlocal operators and hence is not a potential function in the usual sense). The terms in addition to the pseudopotential, representing electrostatic interactions, have been derived in an earlier paper.[2] We will therefore briefly review their properties and show how their definition follows from the form of the pseudopotential.

The computational method based on this theoretical approach allows parellel all-electron and valence-only calculations to be carried out and compared. We report such a study using one-configuration descriptions of Li and Li_2 and a five-configuration description of Li_2. These results demonstrate both the validity of the individual approximations involved in using pseudopotential operators, and also the precision of the overall method.

II. General Theory

The greatest simplification in the description of the valence-electron distribution results if the valence orbitals are allowed to be completely independent of the core, and hence are not required to have nodes in the core region. Therefore in this section we will discuss the conditions that must be met by a set of nodeless spacial functions (pseudoorbitals) in order that they be numerically equal to the equivalent valence canonical molecular orbitals in the valence region. Here valence will be defined as all points in space where the sum of all core orbitals is negligibly small. Note that these conditions alone, rather than consideration of computed properties, lead to the formation of a pseudopotential. For example, a parameterization scheme based on atomic orbital energies might precisely reproduce molecular-orbital energies. But all the properties of a system may in principle be obtained from its wavefunction; and such parameters giving accurate orbital energies may well not suffice for a good estimation of some physically important property. Also, it is nearly always found that when the pseudoorbitals are properly

determined they are sufficiently similar to the true orbitals that many other properties, such as molecular geometries, are also accurately reproduced.

The condition that the total energy obtained by any SCF method be a minimum with respect to spacial variations of an orbital ϕ_k may be written[7]

$$F^k\phi_k - \sum_{j\neq k} \langle\phi_j|F^k|\phi_k\rangle\phi_j = 0 \qquad (1)$$

where F^k is the Fock operator for orbital k. The terms $\langle\phi_j|F^k|\phi_k\rangle$ are Lagrange multipliers that ensure orbital normalization when j = k and orthogonality for $j \neq k$. In these expressions and those below we will use indices j and k to refer to orbitals ordered regardless of symmetry, and m and n within a symmetry block.

In the MCSCF method, the wavefunction is also expanded as a superposition of electronic configurations.[8,9] These are generally obtained by one or a pair of electrons from the Hartree-Fock configuration to excited orbitals, each of which is optimal in the sense that it satisfies its own Fock equation as in Eq. (1). Excitations are chosen as connecting valence orbitals, since electron correlation in the region near the nuclei is of little practical interest. In the total energy found by this procedure, all terms depending solely on the core orbitals appear as an additive constant as the valence orbitals are varied. There is thus a logical relationship between the molecular MCSCF approach and its valence-only counterpart.

The condition that must be satisfied in order that the energy be a minimum with respect to variation of the contributions of all configurations in the wavefunction may be written in the form[9]

$$\sum_n A_{n\sigma}H_{m\sigma,n\sigma} = EA_{m\sigma} \qquad (2)$$

where E is the total energy and $A_{m\sigma}$ is the vector of configuration expansion coefficients of the m^{th} root of H, assumed to be the lowest, of symmetry σ. In forming H one may consider either the requisite integrals over all the orbitals, or equivalently those which involve only valence orbitals. The values of $A_{m\sigma}$ may be shown to be the same in either case; but, in the latter, $E = E_v$ the total energy minus the self-energy of the core. Assume for simplicity that each configuration may be associated with either the Hartree-Fock case or an excitation to a specific higher orbital. Then

$$H_{\sigma m,\sigma m} = N_{\sigma m}(h_{\sigma m} + \sum_{\mu \ell} N_{\mu \ell} P_{\sigma m,\mu \ell}) + d_\sigma K_{\sigma m,\sigma m} \tag{3a}$$

$$H_{\sigma m \mu n} = (d_\sigma d_\mu)^{\frac{1}{2}} K_{\sigma m,\mu n} \quad \text{for } \sigma m \neq \mu n, \tag{3b}$$

where $N_{\sigma m}$ is the occupation number of orbital m, $h_{\sigma m}$ is the one-electron Hamiltonian, d_σ is the dimension of symmetry σ (i.e. 1 for sigma, 2 for pi, etc.) and

$$P_{\lambda m,\mu \ell} = (d_\lambda d_\mu)^{-1}[J_{\lambda m,\mu \ell} - \tfrac{1}{2} K_{\lambda m,\mu \ell}]. \tag{4}$$

Here $J_{\lambda m,\mu \ell}$ and $K_{\lambda m,\mu \ell}$ are the conventional Coulomb and exchange terms connecting the valence orbitals with each other and with the core. The solutions of (1) and (2) are interdependent, since the matrix elements of H depend on the spacial form of the orbitals, and each F^k may be shown to depend on the $A_{m\sigma}$.

In constructing the H matrix in a valence-only calculation, it should be noted that any effective potential employed to simulate the core orbitals is required to be a one-electron operator, so that it modifies only $H_{\sigma m,\sigma m}$ in (3). The off-diagonal terms $H_{\sigma m,\mu n}$ depend solely on the (two-electron) exchange integral $K_{\sigma m,\mu n}$. Therefore $A_{i\sigma}$, the expansion of the wavefunction in

terms of configurations, is independent of the effective potential, except for the indirect dependence through Eq. (1). Any calculation employing one-electron operators to represent the core orbitals must rely on the assumptions that (i) the solutions of Eq. (1) are not sensitive to the values of $A_{i\sigma}$, and (ii) the pseudoorbitals obtained in this way are equal in value to the true orbitals over a sufficiently large region of space, so that two-electron integrals over both sets of functions are approximately the same.

The form of the pseudopotential and effective potential must therefore be found by relying on Eq. (1). Let χ_k be the pseudoorbital derived from ϕ_k by adding an arbitrary linear combination of core orbitals. If P is the core-projection operator,

$$P = \sum_{j=\text{core}} |\phi_j\rangle\langle\phi_j| \tag{5}$$

then

$$\phi_k = (1 - P)\chi_k. \tag{6}$$

Dividing the ϕ_m into core and valence functions, Eq. (1) may be written in the form

$$F^k\phi_k - \sum_{j=\text{core}} \langle\phi_j|F^k|\phi_k\rangle\phi_j - \sum_{\ell=\text{valence}\neq k} \langle\phi_\ell|F^k|\phi_k\rangle\phi_\ell$$

$$= \langle\phi_k|F^k|\phi_k\rangle\phi_k. \tag{7}$$

Partially substituting (6) into (7),

$$F^k(1 - P)\phi_k - \sum_{j=\text{core}} \langle\phi_j|F^k|(1 - P)\chi_k\rangle\phi_j - \sum_{\ell=\text{valence}\neq k} \langle\phi_\ell|F^k|\phi_k\rangle\phi_\ell$$

$$= \langle\phi_k|F^k|\phi_k\rangle(1 - P)\chi_k. \tag{8}$$

Now if we let η_k represent $\langle\phi_k|F^k|\phi_k\rangle$, the diagonal Lagrange multiplier, and use definition (5),

$$F^k(1 - P)\chi_k - PF^k[(1 - P)\chi_k] - \sum_{\ell=\text{valence}\neq k} \langle\phi_\ell|F^k|\phi_k\rangle\phi_\ell = \eta_k(1 - P)\chi_k. \tag{9}$$

After rearranging, this becomes

$$F^k\chi_k + [PF^kP - F^kP - PF^k + \eta_k P]\chi_k - \sum_{\ell=\text{valence}\neq k} \langle\phi_\ell|F^k|\phi_k\rangle\phi_\ell = \eta_k\chi_k. \tag{10}$$

The term in brackets is now the usual form of the generalized Phillips-Kleinman pseudopotential[10] for orbital k. It may be reduced to an expression involving only overlap integrals if it is assumed that the core orbitals are approximate eigenfunctions of each F^k, so that P and F^k commute. In this case the pseudopotential operator becomes

$$V^{PP}(\eta_k) \equiv \eta_k P - F^k P = \sum_{j=\text{core}} (\eta_k - \eta_j)|\phi_j\rangle\langle\phi_j|. \tag{11}$$

This now allows us to form an equation for χ_k analogous to Eq. (1). If we define

$$\bar{F}^k \equiv F^k + V^{PP}(\eta_k) \tag{12}$$

then Eq. (10) may be written in a form in which core-valence Lagrange multipliers do not appear,

$$\bar{F}^k\chi_k - \sum_{\ell=\text{valence}\neq k} \langle\chi_\ell|\bar{F}^k|\chi_k\rangle\chi_\ell = \eta_k\chi_k \tag{13}$$

providing

$$\sum_{\ell=\text{valence}\neq k} \langle\phi_\ell|F^k|\phi_k\rangle\phi_\ell \equiv \sum_{\ell=\text{valence}\neq k} \langle\chi_\ell|\bar{F}^k|\chi_k\rangle\chi_\ell \tag{14a}$$

and

$$\langle \phi_k | F^k | \phi_k \rangle \qquad \eta_k = \langle \chi_k | F^k | \chi_k \rangle \tag{14b}$$

These conditions are generally satisfied in practice within a good approximation. For example, all the terms appearing in (14a) are generally quite small, and vanish in the case of one-configuration methods. Also since valence-only calculations generally reproduce valence orbital energies quantitatively in one-configuration calculations, (14b) is expected to hold at least for orbitals that are not highly excited.

In applying these equations, ϕ_j *and* η_j *for core orbitals may be taken* from readily available reference systems, such as the constituent atoms of a molecule. The χ_k and η_k are then found by solving Eq. (13).

Note that each orbital, including those not occupied in the Hartree-Fock configuration, has its own pseudopotential operator. In conventional MCSCF calculations using a small number of configurations, all orbitals that are completely filled in every configuration share a common Fock operator. Pseudopotential calculations, on the other hand, require a distinct $\bar{F}^k$ operator for each occupied orbital, regardless of its degree of occupation. This does not pose a computational difficulty, however, and the difference in the number of these operators disappears when the number of configurations is large.

Eq. (13) is much more readily solved than Eq. (1) since fewer functions need to be found and these may be described by a much smaller set of basis functions. However, $\bar{F}^k$ contains a large number of two-electron integrals connecting core and valence orbitals. In order to solve (13) it is useful to introduce a set of potential functions, *expressible in terms of one-electron integrals,* to replace them. We have previously described a technique for generating these potentials *for one-configuration* calculations. [2] The same formulas apply in

the multiconfiguration case since, assuming all core orbitals are closed, precisely the same type of core-valence Coulomb and exchange integrals occur.[9]

Eq. (13) must therefore be reformulated in terms of a set of Fock operators $\hat{F}^k$ that depend on the coordinates of only valence electrons. In general $\hat{F}^k$ is to be replaced by $\hat{F}^k + V^{PP}(n_k) + W^k$, where W^k is a one-electron operator whose form is to be determined. It is again necessary to choose a reference system, generally the free atoms, and to assume that once W^k is found for that case it will be transferrable to other systems, such as molecules.

Note that in Eq. (13) the summation vanishes by symmetry for a one-configuration description of an atom.
There are thus three possible ways to define W^k: require that it (i) reproduce the form of $\bar{F}^k$, (ii) reproduce the value of n_k, or (iii) minimize $(\bar{F}^k - n_k)\chi_k$. The second choice may be the most accurate in some cases, since it can compensate for lack of commutivity between F^k and the core orbitals, and it causes condition (14b) to be satisfied by construction. However this method relies on only a small set of distinct numbers, atomic-orbital energies, and hence does not allow a very detailed description of W^k. Choosing its functional form carefully gives good results in many cases, but in general only when small basis sets are employed.[2] The third choice above assumes that Eq. (13) can be satisfied at all points in space. This cannot be true if χ_k is described by a finite linear combination of basis functions. In other words, such a definition makes W^k a sensitive function of χ_k. Further, if greatly differing descriptions of χ_k are used in the atom and molecule, W^k so determined for an atom may not be appropriate to the molecular case.

Therefore, as in our earlier work, we impose the operator-equivalence condition

$$[\hat{F}^k + V^{PP}(n_k) + W^k]\chi_k = \bar{F}^k\chi_k \tag{15}$$

which, from Eq. (10), may be written

$$(\hat{F}^k + W^k)\chi_k = F\chi_k. \tag{16}$$

This is clearly the same as minimizing $(\hat{F}^k - \eta_k)\chi_k$ for large valence basic sets. It will also reproduce η_k provided Eq. (14b) is satisfied, although of course the converse is not true.

An additional advantage of defining W^k in operator form is that Eq. (16) can generate a potential commensurate with any function, rather than only with a specific valence atomic orbital. Suppose for example that χ_k is described by a series of basis functions, ψ_i,

$$\chi_k = \sum_i C_i{}^k \psi_i. \tag{17}$$

There are two ways of determining W^k, which are equivalent for the ground state of an atom but not otherwise. First, W^k may be associated with a particular atomic angular-momentum type, such as s or p. Then Eq. (16) may be solved setting χ_k equal to the atomic pseudoorbital of each type. More generally, W^k may also be determined separately for each member of the basis set,

$$W_i^k = [(F^k - \hat{F}^k)\psi_i]/\psi_i. \tag{18}$$

Using (17) this gives

$$(\hat{F}^k + W^k)\chi_k = \hat{F}^k\chi_k + \sum_i W_i^k C_i{}^k \psi_i = \hat{F}^k\chi_k + \sum_i (F^k - \hat{F}^k)C_i{}^k\psi_i$$

$$= F^k\chi_k. \tag{19}$$

In other words W^k may be considered as being projected either onto each angular-momentum type or onto each basis function, both alternatives satisfying Eq. (16) for atoms.

F^k and $\hat{F}^k$ are of course independent of k in the closed shell Hartree-Fock case. In general all the F^k (and $\hat{F}^k$) operators are quite similar except for highly excited valence orbitals. The difference $(F^k - \hat{F}^k)$ is essentially independent of k in all cases, since it reflects only core electron density. We will therefore drop the k in Eq. (18).

For any other valence function χ_ℓ, which may or may not approximate an atomic orbital, we have

$$(\hat{F}^\ell + W^\ell)\chi_\ell = \hat{F}^\ell\chi_\ell + \sum_i W_i C_i^\ell \psi_i = \hat{F}^\ell\chi_\ell + \sum_i (F^\ell - \hat{F}^\ell) C_i^\ell \psi_i = F^\ell \chi_\ell. \quad (20)$$

Thus the core potential determined in this way would be expected to reproduce to some extent the behavior of excited molecular orbitals such as those formed from excited or ionized states of the constituent atom, even though W^k is generally based solely on ground states of neutral atoms.

Other features of these core potential functions needed to carry out molecular calculations are the same as have been described previously.[1, 2]

Finally, note that specifying the form of the Fock operator is equivalent to setting forth an expression for the total energy. Therefore for consistency the effective potential should modify the other variation condition of the energy, Eq. (2), as well. It may be readily seen that this simply involves adding $V^{PP}(n_{\sigma m})$ to $h_{\sigma m}$ and replacing $P_{\sigma m,\mu\ell}$ by matrix elements of W_i for all core values of $\mu\ell$ in Eq. (3a).

III. Representative Calculations on Li_2

In this section we will examine the accuracy of some of the approximations made above, and illustrate the type of results that are obtained. These will be based on the ground electronic state of Li_2, the simplest molecule possessing core orbitals. It was also one of the first molecules to be extensively studied, by Das, using the MCSCF method.[9] Throughout we will assume an

experimental value of 2.673 Å for the equilibrium bond length.[11] Our basis set is the molecularly-optimized 2-ζ set recently developed by Dixon, Gale and Jordan.[12] For consistency the s-symmetry components of this basis set are used to describe the reference system, the ground ^2S state of the free Li atom.

The W_i functions were generated for each valence basis function as described previously, using Eq. (20) of Ref. 2. The single atomic pseudoorbital is just the valence part of the canonical atomic orbital, that is only the part that depends on 2s basis functions. The core component of each χ_k is fixed by this definition. Note that by using the method described above it is not necessary to postulate the form of a Li 2p orbital in order to form any W_i. For carrying out computations it is convenient to expand each function in the form

$$W_i(r) = 2[1 - \sum_{\ell} d_{i\ell}\exp(-\alpha_{i\ell}r^2)]/r \qquad (21)$$

where r is the distance from the nucleus. The four resulting potential functions in terms of $d_{i\ell}$ and $\alpha_{i\ell}$ for each function ψ_i are shown in Table I.

Our multiconfiguration molecular results are based on the five (six real) configurations that are most significant in terms of both participation in the wavefunction and minimization of the total energy. These are

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$$
$$1\sigma_g^2 1\sigma_u^2 2\sigma_u^2$$
$$1\sigma_g^2 1\sigma_u^2 3\sigma_g^2$$
$$1\sigma_g^2 1\sigma_u^2 4\sigma_g^2$$
$$1\sigma_g^2 1\sigma_u^2 1\pi_u^2$$

where clearly $1\sigma_g$ and $1\sigma_u$ represent the core orbitals. $2\sigma_g$ and $2\sigma_u$ are formed primarily from Li 2s atomic orbitals, $1\pi_u$ from 2p, and $3\sigma_g$ and $4\sigma_g$ from 2p and 3s. At infinite internuclear separation, this set of configurations reduces to the Hartree-Fock description of the free atoms, i.e. $1/\sqrt{2}(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 - 1\sigma_g^2 1\sigma_u^2 2\sigma_u^2)$.

In forming the H matrix we have included all terms, including intra-atomic core-core interactions, in order to allow comparison of E with E_v as descri

The basic assumption in deriving the equation for the effective potential has been that the core is not strongly affected by differences in its environment of valence orbitals. Specifically we require that, to a good approximation, the core orbitals are the same in the atom as in the molecule so that they may be used to construct accurately each $\bar{F}^k$ operator. Further we must postulate the existence of one set of core functions that commutes with each of the F^k. (In Li_2 the last condition does not apply to π orbitals.) A useful measure of the extent to which all these requirements are met is comparison of the diagonal Lagrange multipliers, η_k. As a test of the first condition, we list in Table II the values of η_k for the core orbitals obtained by a conventional SCF calculation on Li, and the commensurate single-configuration and multiconfiguration results for Li_2. As might be expected, all these values are about the same - the major differences being between the atomic and the two molecular calculations.

The general similarity of the core solutions obtainable from valence F^k operators, as required by our second condition above, is well known.[15] But we must also require that atomic core orbitals are approximate eigenfunctions of each F^k. The latter might be referred to as virtual core orbitals, since within the SCF formalism they are not allowed to be occupied. The eigenvalues corresponding to these core $1\sigma_g$- and $1\sigma_u$-type eigenfunctions for the Fock

operators of each of the valence orbitals in the multiconfiguration calculation are shown in Table III. (The π Fock operators possess no such solutions.) The results for the $2\sigma_g$ orbital are very close to those obtained from the $1\sigma_g$ and $1\sigma_u$ shown in Table II. These three would be identical in a one-configuration calculation. They are again quite close to the atomic value. The higher orbitals show a progressive decrease in their core eigenvalues as they become less like atomic 2s orbitals. This difference is small except for $4\sigma_g$. As shown below, the $4\sigma_g$ orbital contributes relatively little to the molecular wavefunction, so that the ability of a pseudopotential to describe it as accurately as the others is not critical. The same would also be true of a larger configuration list, which would include primarily other occupations of the first four valence orbitals ($2\sigma_g$, $2\sigma_u$, $1\pi_u$, and $3\sigma_g$).

The one-electron form of the pseudopotential operator, $V^{PP}(\eta_k)$ as defined by Eq. (11) depends on the differences between core and valence Lagrange multipliers. In Table IV we list the values of η_k for the valence orbitals of Li, and one- and five-configuration descriptions of Li_2. The atomic 2s and molecular $2\sigma_g$ values are about the same, but all those corresponding to excited orbitals are again found to be more negative. Comparing values of Table III with those from the last column of Table IV, there is found to be a roughly parallel decrease in η for both core and valence σ orbitals. This suggests that an approximate pseudopotential
based on atomic core Lagrange multipliers but setting $\eta_k = \eta_{2s}$ of Li for all k would be reasonably accurate in this case, since it would roughly reproduce the differences in η_k seen in the all-electron calculation.

We can also use the values of η_k for valence-orbitals to check condition (14b) in conjunction with the W_i functions by carrying out parallel all-electron and valence-electron calculations. In the latter case we employ Eq. (13), add the analogous effective potential to $h_{\sigma m}$ in Eq. (3a), and define the

configuration list to be just $2\sigma_g$, $2\sigma_u$, etc. The results are shown in Table V, along with the core projection of each valence pseudoorbital, defined as

$$\sum_{j=\text{core}} \langle \chi_k | \phi_j \rangle^2,$$

which measures the extent of its interaction with the core. The agreement with the results in Table IV is good for the $2\sigma_g$ orbital but is again somewhat less satisfactory for the excited orbitals. For $3\sigma_g$ and $4\sigma_g$, however, the overlap with the core is relatively small so that $\hat{F}^k$ is less sensitive to n_k for these orbitals.

We now wish to examine the solution of Eq. (2) in terms of this valence-electron description. In particular we need to varify that the exchange integrals in Eq. (3) calculated over pseudoorbitals form a valid approximation to those obtained using the true orbitals. Table VI shows the configuration-interaction matrix H obtained in these two cases. Clearly the off-diagonal elements defined by Eq. (3) are reproduced with reasonable accuracy. The two matrices are seen to differ by essentially a constant times the identity matrix. This constant represents the self-energy of the core electrons, $E - E_v$, in the all-electron case. It follows that the eigenvectors $A_{m\sigma}$ describing the contribution of each configuration to the total wavefunction should also be approximately the same. This is demonstrated in Table VII. The value of $A_{m\sigma}$ coefficients obtained from the valence-electron calculation are quite accurate for each orbital, including $4\sigma_g$, which however makes only a small contribution (.007) to the wavefunction.

Finally, it is useful to compare the total atomic and molecular energies obtained using an effective potential with those obtained from the equivalent all-electron method. These values as shown in Table VIII for the Li

atom and the one-configuration and five-configuration Li_2 calculations. Comparing the second and third columns, the valence-only results somewhat overestimates the correlation energy, giving .0547 a.u. compared to .0268 a.u. in the all-electron case. However comparing the first and third columns shows that the dissociation energy is quite well reproduced, being .0246 in the former case and .0264 in the latter. The experimental value is .0377. Due to the small number of configurations we have employed, our result is also less than that obtained by the large configuration-interaction calculation in Ref. 12. These authors, using the same basis set, obtain a dissociation energy of .0320 a.u.

IV. Conclusions

In the two preceding sections we have (a) outlined a theoretical approach for computing valence molecular orbitals, (b) demonstrated that the approximations involved are valid, and (c) shown the type of results that may be obtained by its use. Since at present molecular calculations are most readily carried out by the expansion method, it is useful that our approach may be carried out entirely within a particular basis set. This obviates the artificial adjustments that arise in attempting to interface an analytical molecular wavefunction with a numerical (Hartree-Fock limit) atomic calculation, as in the method of Kahn and Goddard.[14] Note also that the calculation of dissociation energies using the method described above does not require consideration of a potential function "tail",[15] which is an artifact of their method. Since we have not vet optimized or parameterized our procedure in any way, it seems likely that doing so could improve its accuracy further. However we feel that such parameterizing is generally unreliable, and would not give constructive results in the long run. Finally, it should be emphasized that our overall valence-orbital procedure is sufficiently efficient that computations on large molecular systems are feasible using this method in its present form.

Table I. Seven-term expansions of the core-valence interaction potentials W_i, for each valence basis function of Li. The form of the expansion is given by Eq. (21) in the text.

2s (ζ = 0.8516)		2s' (ζ = 0.7516)		2p (ζ = 0.9920)		2p' (ζ = 0.7967)	
α_ℓ	d_ℓ	α_ℓ	d_ℓ	α_ℓ	d_ℓ	α_ℓ	d_ℓ
10.3858	0.7309	15.6809	0.5505	17.7308	0.2172	13.0738	0.2332
3.7368	0.5332	5.3980	0.6637	5.4798	0.3525	4.7195	0.3354
1.5077	0.3536	1.8797	0.4544	1.8495	0.2183	1.7106	0.2071
0.3041	0.0905	0.9978	0.0675	0.6904	0.0969	0.7456	0.0163
0.1715	-0.1604	0.5641	0.0543	0.5971	-0.0821	0.2141	0.0292
0.0930	0.1576	0.0364	0.0623	0.3531	0.0293	0.1488	-0.0286
0.0548	-0.0630	0.0048	-0.0615	0.0736	0.0134	0.0725	0.0242

Table II. Core diagonal Lagrange multipliers of Li (1s) and Li_2 ($1\sigma_g$, $1\sigma_u$) in the SCF and MCSCF approximations (a.u.).

Li	
1 configuration	-2.4772
Li_2	
1 configuration	-2.4449, -2.4446
Li_2	
5 configurations	-2.4451, -2.4448

Table III. Virtual core eigenvalues of the four σ-symmetry Fock operators in a five-configuration description of Li_2 (a.u.).

Fock operator	core eigenvalues	
	$1\sigma_g$	$1\sigma_u$
$2\sigma_g$	-2.4459,	-2.4455
$2\sigma_u$	-2.4783,	-2.4781
$3\sigma_g$	-2.5142,	-2.5135
$4\sigma_g$	-3.2480,	-3.1778

Table IV. Diagonal Lagrange multipliers for the valence orbitals of the Li atom and Li_2 molecule in the SCF and MCSCF approximations (a.u.).

	Li	Li_2	Li_2
	1 configuration	1 configuration	5 configurations
2s, $2\sigma_g$	-0.1961	-0.1816	-0.2086
$2\sigma_u$	-	-	-0.3369
$3\sigma_g$	-	-	-0.3324
$4\sigma_g$	-	-	-0.5108
$1\pi_u$	-	-	-0.2995

Table V. Valence Lagrange multipliers, η_k, for each valence pseudoorbital found from an effective-potential calculation on Li_2 using five optimized valence configurations. Also shown is the projection of each function on the core orbitals, as defined in the text.

orbital	core projection	η_k
$2\sigma_g$	0.0447	-0.1934
$2\sigma_u$	0.0644	-0.2980
$3\sigma_g$	0.0141	-0.2987
$4\sigma_g$	0.0293	-0.4825
$1\pi_u$	0	-0.2577

Table VI. Configuration-interaction matrices resulting from a five-configuration description of Li_2 in the valence electron and all-electron approximations. The columns of each matrix are ordered in the same way as the rows. Since these matrices are symmetric, only the bottom half is shown.

configuration	valence-electron case				
$2\sigma_g^2$	-0.3495				
$1\pi_u^2$	0.0408	-0.2285			
$2\sigma_u^2$	0.0446	0.0217	-0.1524		
$3\sigma_g^2$	0.0455	0.0087	0.0188	-0.1582	
$4\sigma_g^2$	0.0151	0.0085	0.0313	0.0156	0.1787

configuration	all-electron case				
[core] $2\sigma_g^2$	-14.8288				
[core] $1\pi_u^2$	0.0414	-14.6564			
[core] $2\sigma_u^2$	0.0448	0.0220	-14.5809		
[core] $3\sigma_g^2$	0.0430	0.0086	0.0160	-14.6082	
[core] $4\sigma_g^2$	0.0143	0.0083	0.0314	0.0133	-14.2847

Table VII. Configuration expansion coefficients of the ground electronic state of Li_2 resulting from valence-electron and all-electron calculations.

configuration	valence-electron	all-electron
[core] $2\sigma_g^2$	0.9333	0.9525
[core] $1\pi_u^2$	-0.2075	-0.1695
[core] $2\sigma_u^2$	-0.1279	-0.1187
[core] $3\sigma_g^2$	-0.1626	-0.1454
[core] $4\sigma_g^2$	-0.0072	-0.0091

Table VIII. Energies obtained for Li and Li_2 resulting from valence-electron and all-electron calculations (a.u.).

	Li	Li_2 (1 configuration)	Li_2 (5 configurations)
valence-electron	0.1786	-0.5171	0.3818
all-electron	-7.3117	-14.8290	-14.8558

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Acknowledgments

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Relativistic Core Binding Energies of Selected Atoms: Comparison with Experiment and Other Calculations

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Single-configuration Dirac-Fock binding energies are reported for K 2p Rb 3p, Cs 3d, Mg 1s, Zn 2p, and Cd 3d as well as for the corresponding levels i cations of these elements and the neighboring rare gases. The results are compared with similar Dirac-Slater and Hartree-Fock calculations, and with experiment. It is found that the calculated binding energies are generally in very good agreement with experiment and are superior to Dirac-Slater and Hartree-Foc results. The relativistic contribution is shown to be significant even for lighter atoms.

Relativistic calculations of atomic core binding energies are now being carried out with increasing accuracy. It has been established that relativistic effects can play a major role in determining the magnitudes of these energies. Comparisons with accurate experimental values remain sparse however, partly because measurements on atoms have until recently been essentially restricted to the rare gases. This situation is now changing due to the availability of data obtained by a number of experimental techniques.[1]

In this study we have selected one subshell in potassium, rubidium, cesium, magnesium, zinc and cadmium and computed the binding energy using the Dirac-Fock program of Desclaux,[2] as the difference between the total energy of the hole state and the neutral ground state ("ΔSCF" method). Where appropriate we have calculated explicitly the energies of electronic states of the ions corresponding to varying J values, although for these cases the splitting is not observable experimentally. The choice of systems for this study was dictated by the availability of experimental values from photoelectron spectroscopy.[3,4] For comparison, we have also calculated the binding energies of the corresponding levels in the rare gases, although most of these binding energies have been computed previously by other authors to a similar degree of accuracy. Finally, we also report the corresponding binding energies in the cations of the metal atoms. Our calculations are compared with other theoretical results and with experiment in an attempt to determine the magnitude of the relativistic contribution in each case. The data are shown in Tables 1 and 2.

First we compare our ΔSCF results with experiment.[3,4] The agreement is very good in general, with most of the discrepancies being 0.7 eV or less. Notable exceptions are the neighboring elements Kr and Rb, where the calculated values are too high by ~3eV.

This is certainly not surprising for the krypton 3p since it is well known that the single-particle description breaks down in this case due to the presence of close-lying doubly-ionized states with energies close to the 3p hole states.[5] Furthermore, although these effects are thought to cease beyond Z = 36, there is some evidence[4] that the rubidium 3p region may exhibit similar features. For the majority of the levels reported here, the Dirac-Fock binding energy is lower than the experimental value. This is to be expected since the primary reason for the discrepancy is the difference between the correlation energy contribution to the ground (neutral) state and the hole state energies. In most cases, more correlation is expected in the n-electron system than in the n-1 system; this results in an increase in the binding energy when the correlation energy is included.

A number of approximate relativistic calculations have been reported, the most extensive being the work of Huang, et al.[6] using the Slater approximation for the exchange integrals. The method used in the present work differs from that of Ref. 6 primarily in that exchange is treated exactly. It is of interest therefore to compare the binding energies obtained by the two methods. This is done in columns 2 and 4 of Table 1 and columns 2 and 3 of Table 2. The Dirac-Slater results are in reasonable agreement with experiment, but generally the agreement is not as good as with Dirac-Fock, as expected. Interestingly, the Dirac-Slater binding energies are invariably lower than the Dirac-Fock binding energies. This is perhaps due to an overestimation of the exchange contribution in the hole state compared to the ground (neutral) state.

Another reason for carrying out these calculations is to compare with analogous nonrelativistic results. Recently Broughton and Bagus[7] reported extensive binding energy results for selected levels of a large number of atoms

and ions. Neither our calculations nor theirs suffer from any basis-set deficiencies, since numerical methods were used in both cases; therefore any differences must be attributed to relativistic effects. A dramatic example of this is the Mg 1s level where the difference amounts to ∿1.9 eV. The accepted explanation is that relativity causes the s levels to contract thus raising the binding energy.[8] All the other levels we wish to compare with the results of Ref. 7 are spin-orbit split, an effect that is of course absent in the non-relativistic calculations. The single level obtained in Hartree-Fock does not truly correspond to an average of the spin-orbit components, as can be seen from examination of the relativistic hamiltonian.[9] Using the non-relativistic hamiltonian as a reference, there is no reason to expect that the two spin-orbit levels should be affected symmetrically by the addition of all the extra terms which account for relativistic effects. We should therefore compare the non-relativistic binding energy to both spin-orbit split levels rather than their mean. For p levels, we note that the non-relativistic result is always closer to the binding energy of the $p_{3/2}$ level while for d levels it more closely resembles the $d_{3/2}$ level. The trend in d levels has been observed previously in our study of cesium and iodine, and their ions.[10] Its origin is simply that in the relativistic case the s and p electrons are more tightly bound than in the non-relativistic approximation, while for d electrons the opposite is true. Thus the less bound of the p and more tightly bound of the d spin-orbit components lie nearest the Hartree-Fock values. The relativistic shift of the spin-orbit pair is often about half the spin-orbit splitting, resulting in a near coincidence of the Hartree-Fock and one of the Dirac-Fock values. Note also that, as expected, the non-relativistic results do not agree as well with experiment as do the relativistic ones, with discrepancies of 2-3 eV in some cases. Particularly interesting is the

nonrelativistic value for the Cs 3d, which is about 4 eV higher than the experimental binding energy. Similar behavior is expected for Xe 3d. The Cd 3d levels show the same effect but to a somewhat lesser extent; here a difference of about 2 eV is observed. In all cases the orbitals either expand or contract in comparison to their non-relativistic approximations depending on their ℓ values, as noted above. Thus care should be exercised in explaining the differences between non-relativistic Hartree-Fock binding energies and experiment since our results clearly show that the correlation energy contribution is not the only source of disagreement even for these lighter atoms. We would expect this to be the case in molecules containing these atoms.

We have also calculated core binding energies of the corresponding positive ions, primarily for comparison with the results of Broughton and Bagus.[7] Although the relativistic and non-relativistic atom-ion shifts are close, they are really not quantitatively the same, indicating that relativistic effects do not cancel out completely in going from the neutral to the ion. In general, the relativistically calculated shift is higher, sometimes by as much as 0.2 eV. This is most likely due to the fact that the valence electrons, being of s symmetry, are more contracted in the relativistic case and therefore more effective in screening core electrons from the nucleus.

Turning to the relaxation energies (the difference between the negative of the orbital energy and the ΔSCF energy) we note that spin-orbit components possess different relaxation energies. This has been noted once before[10] as being clearly due to the added relaxation contribution of the $l + \frac{1}{2}$ component to ionization from the $l - \frac{1}{2}$ level but not the reverse. We also note that the non-relativistic relaxation energies are always lower than the relaxation energies of either of the corresponding spin-orbit components.

It is interesting to compare the relaxation energies in isoelectronic species such as the alkali metal ions and the rare gases. (The results for the latter are shown in Table 2.) In every case the lower-Z species show more relaxation. Similar behavior was noted for the isoelectronic ions Cs^+ and I^-.[10] The explanation probably lies in the more diffuse nature of the orbitals of the lower-Z species thus allowing for more relaxation. An interesting example of this is Mg^{2+} and Ne, where the relaxation energy is about 1 eV less in Mg^{2+} than in Ne.

The calculated core binding energies for the rare gases are in good agreement with experiment except for krypton as noted above. Results very close to ours have been obtained by other workers.[11]

In conclusion, we have shown that single configuration relativistic calculations yield binding energies in very good agreement with experiment for most of the elements considered in this work and that relativistic contribution can be significant even in light atoms.

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TABLE 1

Core Binding Energies and Relaxation Energies (eV)

Level	Binding Energy				Ion-Atom Shift[f]	Relaxation Energy[a]	
	D-S[b]	H-F[c]	D-F[d]	Exp[e]		H-F	D-F
K $2p_{1/2}$	303.00	301.32	303.07, 303.11	303.2		12.14	12.52
K $2p_{3/2}$	300.20		300.38, 300.31	300.5			12.30
K^+ $2p_{3/2}$		308.43	307.47	-	7.13 (7.10)	10.99	11.15
Rb $3p_{1/2}$	257.10	248.94	257.22, 257.25	254.3		9.24	9.93
Rb $3p_{3/2}$	247.86		248.07, 248.01	245.4			9.53
Rb^+ $3p_{3/2}$		255.36	254.54	-	6.51 (6.42)	8.29	8.56
Cs $3d_{3/2}$	745.80	749.67	745.88, 745.89	745.6[g]		18.42	19.46
Cs $3d_{5/2}$	731.88		732.08, 732.07	731.6[g]			18.74
Cs^+ $3d_{5/2}$		755.32	737.88	-	5.81 (5.65)	17.61	17.93
Mg 1s	1310.58	1309.24	1311.10	1311.3[g]		25.02	25.71
Mg^{2+} 1s		1332.36	1334.25	-	23.15 (23.12)	21.95	22.65
Zn $2p_{1/2}$	1051.43	1031.60	1051.73	1052.1[g]		27.62	29.66
Zn $2p_{3/2}$	1028.02		1028.47	1028.9[g]			28.73
Zn^{2+} $2p_{3/2}$		1054.10	1051.18	-	22.71 (22.49)	25.36	26.49
Cd $3d_{3/2}$	417.88	420.55	418.07	418.8		16.80	17.34
Cd $3d_{5/2}$	411.12		411.38	412.0			16.89
Cd^{2+} $3d_{5/2}$		440.14	431.48	-	20.10 (19.59)	15.09	15.20

TABLE 1 (continued)

[a]The negative of the orbital eigenvalue minus ΔSCF energy; the H-F results are from Ref. 7. The D-F results were obtained using the ΔSCF energy averaged over multiplets.

[b]Dirac-Slater ΔSCF results from Ref. 6.

[c]Hartree-Fock ΔSCF results from Ref. 7.

[d]Single configuration ΔSCF Dirac-Fock calculations using the program in Ref. 2. Where two energies are listed, these correspond to states of least (upper) and greatest (lower) J quantum number.

[e]From Ref. 3 for Zn and Cd and Ref. 4 for the rest.

[f]The binding energies used to compute this shift are averaged over multiplets for the atoms. The numbers in parentheses are non-relativistic shifts from Ref. 7.

[g]The experimental values from Refs 3 and 4 were reduced by 0.2 eV in view of the most recent experimental Nels value of 870.21 eV (see Table 2); this is the level used to calibrate the spectra.

TABLE 2

Core Binding Energies and Relaxation Energies for the Rare Gases (eV)

Level	Binding Energy			Relaxation Energy
	D-S[a]	D-F[b]	Exp	D-F
Ne 1s	869.15	869.47	870.21[c]	23.55
Ar $2p_{1/2}$	249.95	250.28	250.78[d]	11.82
Ar $2p_{3/2}$	247.80	248.16	248.63[d]	11.63
Kr $3p_{1/2}$	224.82	225.01	221.8[e]	9.55
Kr $3p_{3/2}$	216.81	217.03	214.2[e]	9.17
Xe $3d_{3/2}$	688.81	689.03	689.35[e]	19.11
Xe $3d_{5/2}$	676.16	676.47	676.70[e]	18.44

[a]From Ref. 6.

[b]Present work.

[c]From H. Ågren, J. Nordgren, L. Selander, C. Nordling, and K. Siegbahn, J. Electron Spectrosc. 14, 27 (1978).

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[e]From Ref. 5.

APPENDIX D.

Symmetries of Transition States in Isoenergic Reactions

Sir:

Several authors have shown that transition states (TS) of chemical reactions must possess unique symmetry properites. A systematic set of rules have been put forth by McIver and Stanton[1], who stated for example that a transition vector can not correspond to a degenerate vibrational mode. However the special case of isoenergetic reactions, in which products and reactants have the same energy to a high level of approximation, gives rise to an additional and powerful set of symmetry constraints which have apparently not previously been considered. Most reactions are not, of course, isoenergetic. Perhaps the most common examples of this type of process are isotopic exchange reactions and molecular rearrangements between energetically equivalent conformations. In this paper the symmetry condition that governs isoenergetic reactions is derived and applied to three- and four- center mechanisms. Specific application is then made to representative examples of the two kinds of reaction mentioned above.

It will be assumed throughout that the transition state corresponds to a maximum in the energy along the reaction coordinate, and is unique. It is then straightforward to show that the point group of the nuclei in the TS must contain at least one symmetry operation. If products and reactants are of equal energy, the forward and reverse directions along the reaction coordinate must be energetically equivalent. The vibrational mode of the TS that represents reaction in these two directions must be symmetric, so that the Taylor series expansion of the energy in terms of the reaction coordinate may have no odd contributions. Odd terms may appear only if they are totally symmetric under all the symmetry operations of the group[2]. However if the TS had no symmetry, then every vibration would be totally symmetric. Hence the vanishing of odd terms in the energy implies at least one symmetry operation.

Not every vibration of the TS, regardless of symmetry, will necessarily lie along the reaction coordinate. It is necessary to also specify what groups of atoms represent products and reactants. In the case of isoenergetic reactions it is clearly necessary that there be two ways of grouping atoms as products and reactants that are symmetrically equivalent, so that the vibrations separating them will be energetically equivalent. For example consider the reaction A_1–A_2 + A_3 → A_1 + A_2–A_3. Symmetrically equivalent groupings in the TS are [(A_1,A_2),(A_3)] and [(A_1),(A_2,A_3)]. Thus, the bonds A_1–A_2 and A_2–A_3 must be equal and the TS has C_{2v} symmetry. This is also what one would expect intuitively.

Now consider a reaction involving four centers. In this case the result is less intuitively apparant. For the reaction A_1–A_3 + A_2–A_4 → A_1–A_2 + A_3–A_4, symmetrically-equivant groups of centers A_1, A_2, A_3 and A_4 are [(A_1,A_2),(A_3,A_4)], [(A_1,A_3),(A_2,A_4)] and [(A_1,A_4),(A_2,A_3)]. A minimum of two of these groups must be symmetrically

equivalent, say the first two. In this case bond A_1–A_2 and A_1–A_3 are equal, as are A_3–A_4 and A_2–A_4 (or equivalently A_1–A_2 and A_2–A_4, A_3–A_4 and A_1–A_3). Again, a TS of C_{2v} symmetry is obtained, with the vertical symmetry plane passing through precisely two atoms. It is important to note however that the symmetry of this TS is not unique to this reaction. Thus for the reaction A_1–A_2–A_3 + A_4 → A_1 + A_2–A_3–A_4 there are four possible symmetrically equivalent groups: [(A_1,A_2,A_3),A_4], [(A_1,A_2,A_4),A_3], *etc.*. Two of these groups must be equivalent, say the two given. Now there are two distinct possibilities: A_1–A_2 = A_2–A_4 and A_2–A_3 = A_1–A_2; or A_2–A_3 = A_2–A_4 and A_1–A_2 ≠ A_1–A_2. It may be seen that, depending on the way in which the equivalent groups are chosen, a TS of either C_{2v} or C_2 symmetry may result.

An example of an isoenergetic reaction that has been widely studied is H_2 + D_2 → 2HD which, on the basis of experimental data[3], has been thought to proceed via a bimolecular mechanism. The symmetries of the possible paths for this reaction have been studied by Wright[4] and Silver[5], who however did not consider its isoenergetic properties. A large number of putative TS constrained to be of a particular symmetry have been computed theoretically, most of which possess the C_{2v} symmetry required by the above arguments. These include the square[6,7,8], tetrahedron[6,7,10], rhombus[6], kite[6,8], Y[8] and T[9]. However the rule derived above excludes two of the conformations which are the most favorable energetically: the trapezoid[6,8] and linear chain[6,7,11]. Also excluded are the rhomboid[6,7] and rectangle[8] among others, and the completely asymmetric case[5]. Another interesting example is the interconversion between the two possibile rectangular conformations of cyclobutadiene and its singly-charged ions. This process is currently thought to take place in the plane of the molecule and to pass through a square conformation[12], although few other alternatives been studied thus far. For rearrangements of this type the same rule applies and the TS must have at least kite symmetry.

The requirement that there be symmetrically equivalent groups in the TS of an isoenergetic reaction, along with other rules governing nuclear and orbital symmetry, are fairly restrictive and may uniquely determine the TS in many cases. In computing activation energies by *ab initio* methods, one need only optimize a molecular geometry of the minimum symmetry. If a bound species is obtained in this way, it provides a direct estimate of the activation energy. If a bound species is not obtained, it implies that the proposed mechanism is incorrect.[13].

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13. However the reverse is not true; finding a bound TS does not necessarily support a postulated mechanism. For example we have computed the minimum-symmetry TS for $H_2 + D_2$ exchange using both SCF and MCSCF methods. In the first case, spurious bound states are found but in the latter, more accurate calculations, these are unbound with respect to a molecule and two atoms. See M. J. Rothman, L. L. Lohr, Jr., C. S. Ewig, and J. R. Van Waser, *Potential Energy Surfaces and Dynamics Calculations*, (plenum, New York, 1981), 653.

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Abstract

A technique for determining the symmetries of transition states of isoenergetic reactions is proposed, and applied to the possible three- and four-center mechanisms. Specific examples given are the exchange of a H atom between two H_2 molecules, and the rearrangement of the cyclobutadiene molecule.

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