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The primary objective of developing improved techniques for calculating the electronic structure of clusters on the basis of density functional theory was accomplished. The methods are the most accurate presently available. The most important topic which is not yet treated satisfactorily in our approach or in any of the competing methods is that of embedding the cluster, i.e., treating its environment properly. New results were obtained for several interesting systems.

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CLUSTERS OF TRANSITION METAL ATOMS

FINAL TECHNICAL REPORT

J. Callaway, Principal Investigator

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Scientific Problem and Results

The primary emphasis of the work performed was the development and application of accurate methods of calculating the electronic structure of atomic clusters, particularly of transition elements. In order to support this work, some attention was devoted to investigations of the local spin density approximation which underlies our studies.

The following discussion of results refers to the papers we published by number.

Papers 1,3,10; Applications to Molecules. We thought it to be important to test our calculational procedures which were intended to be applied to large clusters on some molecules which are reasonably well understood experimentally. Paper 3 demonstrated that reasonable results are obtained for the heteronuclear diatomic molecules LiH, CO, and NO. This work employed an adaption of the standard quantum chemistry program GAUSS76 to use the local spin density approximation. The results demonstrate the superiority of the LSDA results to Hartree Fock for quantities like the internuclear distance, dipole moment, and lowest vibrational frequency. However we found the quantum chemistry program to be very difficult to modify in a way to enable calculations for the large clusters of interest, and abandoned this approach in favor of developing our own program package.

Paper 8 reports an investigation of the SF_6 molecule. This work used our own cluster program. The SF_6 molecule was chosen for study because it is of reasonable size and because its octahedral shape is suitable for our programs. We found, as usual, rather good results for the binding energy and internuclear distances. Ionization potentials and electron affinities were computed. The formation of the negative ion, SF_6^- was found to involve a

significant amount of nuclear relaxation. The results are, for most of the properties studied, superior to those obtained in the Hartree Fock approximation.

Papers 6,14; Developments of Density Functional Theory. In paper 6, the explicit temperature dependence of the exchange correlation potential in the local spin density approximation was calculated. This was a rather straightforward application of temperature dependent many body perturbation theory. The temperature dependence was found to be quite weak for temperatures relevant to solid state physics.

Paper 14 uses the aluminum atom, in all stages of ionization, as a test case to compare different approximate exchange correlation potentials which have been proposed. Ionization potentials were calculated using the transition state method. All exchange correlation potentials (except X_α) give comparably good results; X_α is significantly worse. In the course of this work it was demonstrated that the total energy of a neutral atom can be accurately calculated by summing the ionization potentials of the various states of ionization calculated by the transition state method.

Papers 2,4,5; Clusters of Iron and Nickel. These papers contain our most important results. We developed a new method of calculating structure of free atomic clusters using the self consistent, spin polarized, local density approximation. A large basis of independent (or contracted) Gaussian orbitals is employed. The calculation is kept to manageable size through the use of symmetrized combinations of these functions.

Iron and nickel clusters (Fe_9 , Fe_{13} , Fe_{15} , Ni_{13} , Ni_{19}) were investigated. The geometry was assumed to be that of the corresponding bulk metal. The most significant result is that the density of states in these clusters, which contain a central atom and one or two shells of neighbors, resembles that

obtained in band calculations quite reasonably closely. This is possible because the d wave functions are quite localized and there are appreciable interactions only between an atom and its first and second neighbor both in the cluster and in the bulk. So, provided the geometry is the same as that of an equivalent of bulk material, a cluster of 15 atoms has already developed a rudimentary band structure.

Of course, there are differences. The calculated magnetic moment per atom in the iron clusters are nearly $3\mu_B$, roughly 40% larger than the bulk value. This occurs because most atoms in these small clusters are surface atoms, and the moment of an iron atom increases as the number of near neighbors decreases. In addition, the spin density distribution is predicted to be different in the cluster than in the bulk: the majority spin electrons prefer the outer atoms; the minority spin electrons prefer the center.

The spin distribution has not been tested. Free iron clusters have been found to be magnetic with moments roughly of $3\mu_B$ per atom in agreement with the calculation. One other experimental observable is the ionization potential. We calculate this quantity by the transition state method; and find fairly good agreement with experiment, including the proper deviation from a monotonic trend connecting atom and bulk. We think this indicates that the most significant uncertainty in these calculations, that of the actual arrangement of atoms in free iron clusters, does not affect our results as much as might be anticipated.

Papers 7,8,11,16; Cluster Models of Alloys. One of the objectives we had in undertaking the development of procedures for calculating the electronic structure of clusters was to find a way to study alloy or defect systems more accurately. It had been concluded from a previous project (supported by ARO), concerning the modification of the electronic structure of aluminum produced

by an atomic vacancy, that accurate self consistency was of the utmost importance if quantitative results were ever to be obtained. Use of a cluster model seemed to be the most practical way to address the problem of self consistency.

Our most important results concern transition metal impurities in copper. We studied 19 atom clusters ($M Cu_{12} Cu_6$; $M=Cr, Mn, Fe, Co, \text{ and } Ni$). All have the central impurity atom surrounded by first and second neighbor shells of copper atoms in the (bulk) f.c.c. atomic geometry. A similar calculation was made for the system $MnAl_{12}Al_6$.

It would require too much space to summarize the results in detail here. The most important is that all of these systems are found to be magnetic, i.e., the density function calculation predicts the existence of a local moment on the transition metal atom. In several cases (Cr, Mn, and Fe in Cu) the magnitude of the local moment is in good agreement with experiment. [Comparison with experiment is not simple in some cases because the Kondo effect can render a local moment unobservable at temperatures below the Kondo temperature, T_K]. Hybridization between the transition metal d orbitals and those of Cu turns out to be large, much more so than is anticipated in the conventional Anderson model approach. When our results are compared with those obtained by other theoretical approaches, we find generally good agreement with Green's function impurity calculations, but poor agreement with scattered wave- X_α calculations. (We think the geometric approximations of the MSW- X_α method may be severe).

Our recent calculation concerning Mn in Al is of interest because the existence of an observable local moment on Mn seems to depend on the local environment. In particular, there seems to be a local moment on Mn in the quasicrystalline phase. Our calculations, made for f.c.c. geometry, show a

modest local moment, but there is substantial screening of the moment by opposing spin polarization on the A_z atoms. The extent to which local density calculations are capable of showing Kondo screening is not clear at this point, and this remains an interesting questions for future study.

Papers 9,12,13,15; Other Cluster Calculations. We reported calculations by density functional and other technique for several other systems. The Hubbard model was studied by exact diagonalization for a variety of small (four and five atom) clusters. We could determine the minimum energy exactly for different geometries. The results are in accord with elaborate quantum chemical calculations where comparison is possible. This approach is capable of great extension to apply to many molecules, but we lack the resources to proceed in this direction.

We have been quite interested in using the density functional approach to study the electronic structure of materials in which localized excitations are possible. This has been one of our objectives from the beginning. The point is that transition state methods are applicable if excitations are localized. We studied the NiO_6^{10-} cluster in this way as an example of an antiferromagnetic insulator. The most important results have been obtained for the high T_C superconductor $YBa_2Cu_3O_7$. We investigated a cluster model of the linear Cu-O chains which are present in this material but not in the 40°K superconductors based on La_2CuO_4 . We were able to show that the shift of peaks in the photoemission spectra to lower energy in comparison to results of band calculations is a consequence of electronic relaxation in the final state. In addition, we could calculate an effective Hubbard interaction parameter which is in agreement with experiment. Much more can be done on this problem.

In summary, our primary objective of developing improved techniques for

calculating the electronic structure of clusters on the basis of density functional theory was accomplished. We believe that our methods are the most accurate presently available. The most important topic which is not yet treated satisfactorily in our approach or in any of the competing methods is that of embedding the cluster, i.e., treating its environment properly. New results were obtained for several interesting systems, as described above and in more detail in the papers we published, which show the power of our methods. It is with much regret that we terminate this work for lack of continuing support.

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