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Brett I. Dunlap	WU: 61-M193-X-0

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Isomers of pure Fe_{13} and icosahedral $Fe_{12}X$ clusters are studied using the all-electron linear-combination-of-Gaussian-type-orbital (LCGTO) local-density-functional (LDF) methods that allow the spin and geometry of the cluster to be determined self-consistently. The Fe_{13} ground state is icosahedral. The icosahedral cluster also has the greatest magnetic moment because of increased symmetry-required orbital degeneracy for electrons of different spins. The central atom of the icosahedral iron cluster has been varied to optimize the spin of the cluster.

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Symmetry and Ferromagnetic Clusters

Brett I. Dunlap

Theoretical Chemistry Section, Code 6119

Naval Research Laboratory

Washington, D.C. 20375-5000, U.S.A.

Tel: (202) 767-3250

Fax: (202) 404-8119

ABSTRACT

Isomers of pure Fe_{13} and icosahedral $Fe_{12}X$ clusters are studied using the all-electron linear-combination-of-Gaussian-type-orbital (LCGTO) local-density-functional (LDF) methods that allow the spin and geometry of the cluster to be determined self-consistently. The Fe_{13} ground state is icosahedral. The icosahedral cluster also has the greatest magnetic moment because of increased symmetry-required orbital degeneracy for electrons of different spins. The central atom of the icosahedral iron cluster has been varied to optimize the spin of the cluster keeping the orbital contribution to the magnetic moment quenched. Varying the central atom under this constraint can alter the magnetic moment by more than 20%. Similar studies have begun on 55-atom icosahedral iron clusters.

The Linear-combination-of-Gaussian-type-orbitals (LCGTO)[1] local-density-functional (LDF)[2] ground state geometry of the 13-atom iron cluster has approximate icosahedral (I_h) symmetry[3] as does the 13-atom nickel cluster[4]. Zero and low magnetic moment, nontransition-metal elemental 13-atom clusters are also icosahedral if directional bonding is not too important[5-6]. The icosahedral 13-atom cluster has two symmetry-inequivalent sets of atoms, a unique central atom surrounded by twelve symmetry equivalent atoms each occupying the corners of an icosahedron. Thus either of these two sets of atoms can be replaced by sets of atoms of a different element without changing the symmetry of the clusters. This work considers the effect of the identity of the central atom on the stability and magnetic moment of the cluster as a whole, and how this approach can be extended to larger icosahedral clusters that have more symmetry-inequivalent shells, which would afford greater possibilities of alloying within the constraint of icosahedral symmetry. This high symmetry can be used to enhance the magnetic moment of these clusters.

The Gaussian orbital basis set for iron was a 15s/11p/6d primitive basis[7] contracted according to an atomic calculation 3,5/2,3/1,3, where for each orbital angular momentum the first number is the number of lowest-energy atomic orbitals ($1s$ to $3s$, etc.) and the second number is the number of most diffuse Gaussians used in the cluster calculations (5 s-type, etc.). Compatible primitive Gaussian basis sets from a handbook[8] were augmented with a single d polarization function[9] (f polarization functions on transition metal atoms in compact structures lead to numerically singular overlap matrices[4]) and every exponent greater than 10 bohr^{-2} contracted. For sulphur this approach lead to a 12s/9p/1d basis orbital basis set which was contracted 2,3/1,4/0,1. The Perdew-Zunger[10] LDF was used. During the self-consistent-field (SCF) process each one-electron energy level was exponentially broadened by 0.025 eV and then occupied from the lowest energy up to a single self-consistent Fermi energy, ϵ_F, for both spins[4].

The number of unpaired spins as a function of the distance between the two symmetry-inequivalent atoms in the I_h Fe_{13} cluster is plotted in Fig. 1 and compared with similar curves for two less stable Fe_{13} structures. The O_h structure is the cuboctahedron, which is a compact portion of the fcc crystal lattice. The D_{3h} structure can be obtained from the fcc cluster by rotating any triad of nearest-neighbor surface atoms by 60° about their center. This third cluster is a compact portion of the hcp lattice. Each surface atom of the hcp and fcc clusters sees an identical nearest-neighbor environment. Therefore these two less stable clusters would be expected to have similar properties. Furthermore, these three cluster have the same equilibrium radial bond distance of 4.4 bohr[2]. Nevertheless, Fig. 1 shows that these three clusters have quite different spin properties. For most radial bond distances the cluster magnetic moments are related,

$$\mu_{I_h} \geq \mu_{O_h} \geq \mu_{D_{3h}}. \tag{1}$$

This difference has been attributed to different symmetry-required degeneracy in these clusters[3]. The average degeneracy of an irreduceable representation (IR) of the icosahedral (I_h), octahedral (O_h), and D_{3h} point groups are 3.2, 2, and $1\frac{1}{3}$, respectively. Furthermore, the maximal degeneracy of IRs of these groups are 5, 3 and 2, respectively. The optimal spin for each cluster changes quite abruptly as a function of radial bond distance for these three clusters because the room-temperature level-broadening parameter is small compared to the average spacing between the one-electron energy levels of at least one spin. For example a jump of 10 units between 4.5 and 4.6 bohr is required for the I_h cluster because the highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) have opposite spin, h_g and h_u orbital symmetry, and reverse their order in energy as the radial bond distance changes from 4.5 to 4.6 bohr. Beyond the plateau reached at largest bond distances

in this figure, the spin-polarized core d electrons reduce their overlap and ferromagnetic ordering may cease.

Fe_{13} deviates slightly from perfect I_h geometry through the Jahn-Teller mechanism. The HOMO of minority spin is a five-fold degenerate h_u orbital that is occupied by only a single electron. If the symmetry unique central atom is removed, an icosahedral shell of 12 iron symmetry-equivalent atoms remains. This I_h shell has 38 unpaired spins and a radial bond distance of 4.2 bohr, yielding a radial contraction of 0.2 bohr upon removal of the central atom. Thus the net spin of the central atom is opposite that of the shell. This and other comparisons are made in Table 1, where the binding energy is defined as the total energy of the 13-atom cluster minus the energy of the shell and an isolated central atom. These energies are computed in (spatial) symmetry-restriced fashion[11].

The size of the hole left inside a I_h-symmetric Fe_{12} shell can be computed two ways—using Slater atomic radii or the shell nearest-neighbor distance. The Slater atomic radius[12] for iron is 1.40Å(2.65 bohr), leaving a hole of radius 0.82Å(1.55 bohr) vacant in the center of the Fe_{12} shell. The nearest-neighbor distance of two atoms in the spherical shell is 105.15% of its radius. Subtracting half of this nearest-neighbor distance from the shell radius yields a hole radius of 1.05Å(1.99 bohr). The small size of this central hole and the fact that the shell lacks two electrons from having completely filled or half-filled shells suggest investigating divalent atoms that are smaller than iron as interesting candidates for filling that hole. Table 1 is heavily weighted with such atoms. From this table, the energetically most favorable such atom is zinc, the cluster containing which has 40 unpaired spins. Indeed it is the most stable cluster found in this study. The highest spin system found is $Fe_{12}S$, but it is energetically less stable than $Fe_{12}Zn$, although more stable than the pure Fe_{13} cluster. If $Fe_{12}O$ has a slightly larger radial bond distance it too would have 44 unpaired spins and be stable against the Jahn-Teller mechanism. Interesting

semiclosed-shell nondivalent systems are $Fe_{12}Al$ and $Fe_{12}Mn$. The former has high spin, 41 unpaired spins, and the latter has low spin, 35 unpaired spins.

Clearly these 13-atom I_h systems are rich in their magnetic properties and thus could potentially be tailored for enigineering applications. Larger highly symmetric systems would afford greater flexibility. Studies of larger systems, specifically the Fe_{55} I_h and Fe_{51} O_h (bcc) clusters, are under way.

With larger magnetic systems the problem of double SCF convergence (simultaneously optimizing the one-electron orbitals and the number of unpaired spins) looms larger. A possible simplification in this effort is to change from using a spin unrestricted (ULDF) formulation of the problem to a restricted open-shell (ROLDF) formulation. Rather than direct optimization of the ROLDF problem, which in general leads to off-diagonal entries in the one-electron eigenvalue matrix, $\underline{\epsilon}$, an average of the local potentials for both spins weighted by the number electron for each spin was used,

$$\epsilon_i \, \phi_i(\mathbf{r}) = [-\tfrac{1}{2}\nabla^2 + \tfrac{N_\uparrow V_\uparrow(\mathbf{r}) + N_\downarrow V_\downarrow(\mathbf{r})}{N_\uparrow + N_\downarrow}]\phi_i(\mathbf{r}), \qquad (2)$$

where the arrow subscripts denote the two spins and N and $V(\mathbf{r})$ are the number of electrons and local potential. For Fe_{13} the two methods yield the same ordering of the one-electron levels and thus the same number of unpaired spins. For I_h Fe_{55}, with the nearest-neighbor distance between shells fixed at 4.4 bohr (the optimal distance for Fe_{13}, but likely too short for larger systems, thus underestimating their magnetic moments) Figs. 2 and 3 give the ROLDF and ULDF eigenvalue spectra. Both calculations yield the same number of unpaired electrons, 64, but the spectra and level ordering are slightly different. The ROLDF approximation does not significanly improve the SCF process, despite stabilizing the orbitals of minority spin near the Fermi energy. Nevertheless, because more than a hundred iterations are needed to reach

an acceptable level of convergence, the ROLDF saves almost a third of the computer time.

Symmetry can have a significant effect on the magnetic moments of small clusters. Currently this effect is most easily addressed theoretically; thus it is important to extend theoretical methods to reliably and economically treat larger clusters.

Acknowledgments

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TABLE

Table 1. Stability, size, and magnetic moments for selected central atoms in an icosahedral $Fe_{12}X$ cluster. The binding energy is in hartrees and radial bond distance in bohr. An up arrow subscript on the highest open-shell spin-orbital indicates that it is occupied by majority-spin electrons.

Central atom	Binding energy	Radial bond distance	Unpaired electrons	Open-shell electrons	Open-shell orbital
None	0.000	4.2	38	3	$h_{g\uparrow}$
Be	0.178	4.3	40	0	–
O	0.118	4.3	42	4	$h_{g\uparrow}$
Mg	0.010	4.5	40	0	–
Al	0.145	4.4	41	0	–
Si	0.258	4.4	40	0	–
S	0.053	4.5	44	0	–
Ti	0.262	4.5	38	2	$h_{g\downarrow}$
Mn	0.206	4.5	35	0	–
Fe	0.006	4.4	34	1	$h_{u\downarrow}$
Ni	0.211	4.4	38	3	$h_{g\uparrow}$
Zn	0.372	4.4	40	0	–
Se	-0.046	4.6	38	3	$h_{u\downarrow}$
Pd	0.109	4.6	38	3	$h_{g\uparrow}$

FIGURE CAPTIONS

Figure 1   The optimal number of unpaired spins as a function of radial bond distance for the hcp (long-dashed curve), fcc (solid curve), and I_h (short-dashed curve) Fe_{13} clusters.

Figure 2   Comparison between the a) restricted open-shell and b) unrestricted one-electron eigenvalue spectra for I_h Fe_{55}. In each panel the majority-spin spectra are to the right of the minority-spin spectra. Both methods give the same number of unpaired electrons, 64, which is fixed by the large gap in the minority-spin spectra at the Fermi energies.
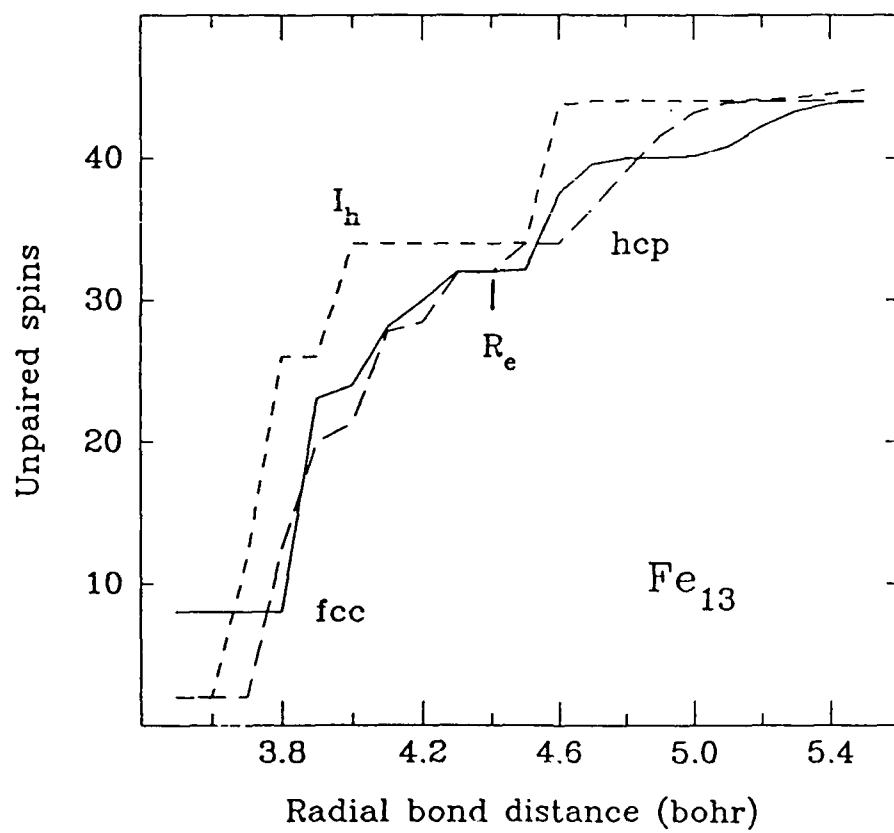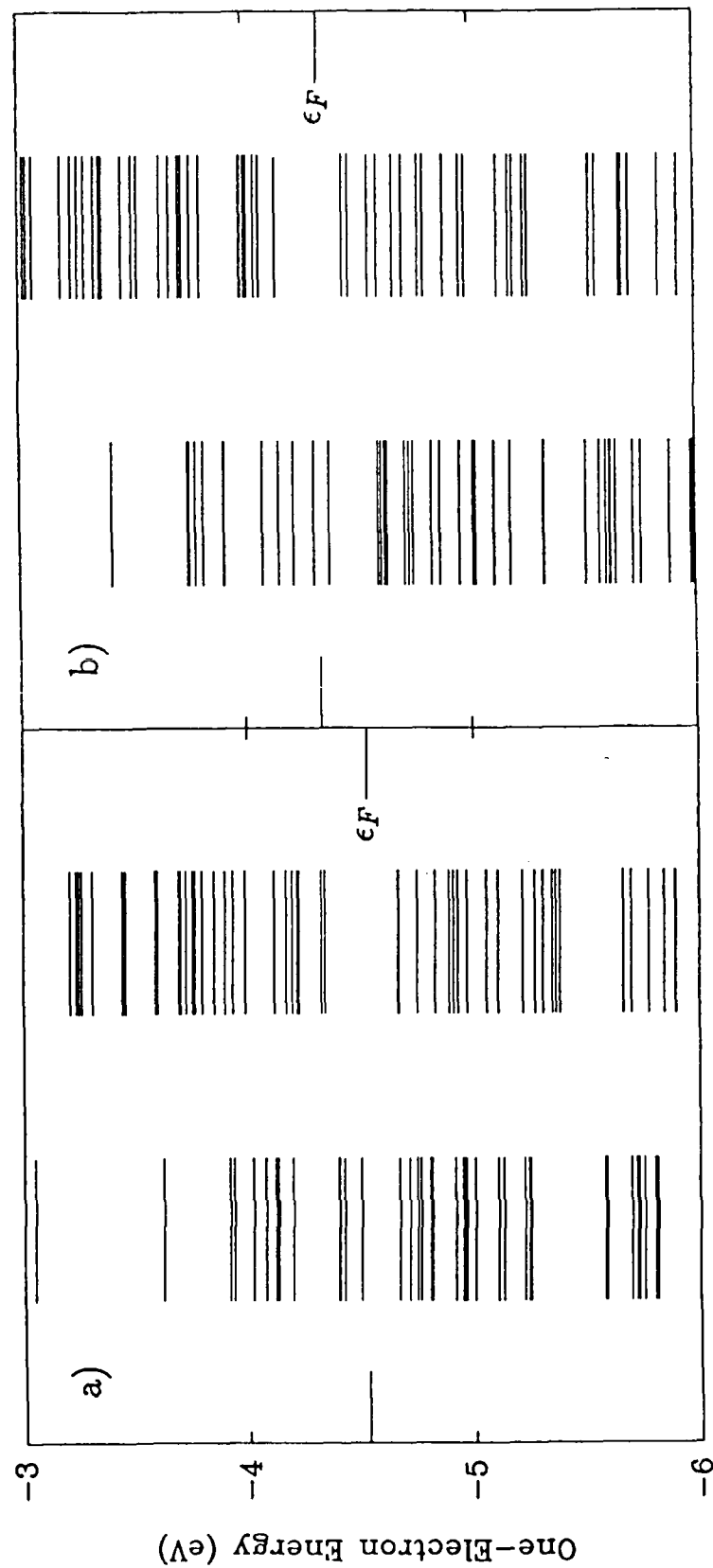
Fig. 1

Fig. 2

ROLDF Icosahedral Fe$_{55}$

ULDF Icosahedral Fe$_{55}$

a)

b)

ϵ_F

ϵ_F

One-Electron Energy (eV)

-3

-4

-5

-6

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Brett I. Dunlap

Theoretical Chemistry Section, Code 6119
Naval Research Laboratory
Washington, D.C. 20375-5000

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Canada

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Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
  Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Bernadette Eichinger (1)
Naval Ship Systems Engineering
  Station
Code 053
Philadelphia Naval Base
Philadelphia, PA 19112

Dr. Sachio Yamamoto (1)
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University of North Carolina
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Salt Lake City, UT 84112

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Department of Chemistry
Bowling Green State University
Bowling Green, OH 43402

Professor Michael Zerner (1)
Department of Chemistry
The University of Florida
Gainesville, FL 32611

Dr. T. Pavlopoulous (1)
Naval Ocean Systems Center
Code 521
San Diego, CA 92152-5000

Dr. Peter P. Schmidt (1)
Chemistry Division, Code 1113PS
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Larry R. Cooper (1)
Electronics Division, Code 1114SS
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

Dr. George B. Wright (1)
Electronics Division, Code 1114SS
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

Defense Technical Information Center (4)
Cameron Station
Alexandria, VA 22314