A FIRST PRINCIPLES STUDY OF CU CLUSTERS

Aninda Jiban Bhattacharyya, Abhijit Mookerjee
S.N. Bose National Centre for Basic Sciences,
JD Block, Sector 3, Salt Lake City,
Calcutta 700091, India

and

A.K. Bhattacharyya
Department of Engineering,
University of Warwick, Coventry CV47AL, U.K.

Abstract

In this communication we study the equilibrium shapes and energetics of Cu clusters of various sizes up to 20 atoms using the Full-Potential Tight Binding Muffin-tin Orbitals Molecular Dynamics. We compare our results with earlier works by physicists and chemists using different methodologies.

1 Introduction

Many of the first principles molecular dynamics approaches to the study of clusters depend upon the construction of suitable pseudopotentials for the constituent atoms. Transition metal clusters require perhaps, alternative treatments ([28, 29, 15]). The deep potentials associated with their d-orbitals are not particularly amenable to the pseudopotential approach. In this communication we shall describe a study of Cu clusters using a full-potential LMTO based molecular dynamics.

Experimentation on the electronic and cohesive properties of transition metal clusters have been extensive [18, 20, 25, 31, 34, 38, 39, 41, 42, 43, 70]. The smaller Cu clusters have been exhaustively studied by quantum chemists [1, 4, 5, 6, 10, 11, 12, 14, 15, 17, 30, 49, 53, 54, 55, 61, 65, 66, 76, 77]. An excellent early review of the field has been made by Ozin [64]. The main issues addressed in these works were: whether small clusters had characteristics of bulk metals and in what way they differed from them in respect to cohesive energies, ionization potentials and magnetism. Recently Apai et al [8] conducted EXAFS studies of Cu clusters supported on carbon. Similar studies of Au and Ag clusters were carried out by Balerna et al [16] and Montano et al [59]. These studies indicate, as one would expect for these metals, that the localized d-electrons play an important role in the
electronic structure. Hence, the $d$-states and their interactions with the extended $s$-states need to be carefully accounted for in a proper theoretical treatment of these materials.

We may classify the theoretical approaches into five groups:

(i) In the first group are the Hartree-Fock and $X\alpha$ descriptions ([66]). In this class we have the self-consistent-field-$X\alpha$ ([53]), the ab-initio self-consistent-field (SCF) using model potentials ([15]) and the SCF with relaxation effects ([58, 76]).

(ii) In the next group are the methods based on the local spin density (LSDA) both without and including self-interaction corrections ([79]). Salahub and coworkers have argued that it is essential to include the gradient corrections in the LSDA in order to treat clusters properly ([22, 32, 33, 36, 69, 71]) since the bonding charge density in a small cluster is highly inhomogeneous.

(iii) The third group includes tight-binding type methods. These include the extended Hückel methods ([7, 12, 13]), re-parameterized Hückel with the Wolfsberg-Helmholtz approximation for the off-diagonal terms ([54]) and those with more flexible forms for them ([3, 46]). This group also has the linear combination of atomic orbitals based SCF methods ([26]). We also have the empirical tight-binding (TB) or the Linear Combination of Atomic Orbitals (LCAO) methods ([27, 28]). These are at best qualitative, since the assumption of transferability of the Hamiltonian parameters is definitely of questionable validity.

(iv) In the fourth group we have the effective potential methods which include the embedded atom pair and many-body potentials ([24, 67]) and the effective medium theory ([27, 44]) with one-electron correlation included ([19, 23, 78]). The equivalent crystal theory (ECT) ([72, 73, 74]) also belongs to this class of empirical potential methods and is capable of dealing with very large clusters.

(v) Finally we have attempts at using the tight-binding linearized muffin-tin orbitals (TB-LMTO) method ([52]) coupled to simulated annealing. In the application of this method to clusters there are several outstanding problems. The treatment of the interstitial region outside the muffin-tin spheres centered at the atomic positions is difficult. Unlike the bulk, where the interstitial region is small and inflating the muffin-tins to slightly overlapping atomic spheres can do away with the interstitial altogether, for clusters this is certainly not so. As the atoms move about, the atomic spheres may not overlap and the interstitial contribution is significant. One may try to overcome this by enclosing the cluster with layers of empty spheres carrying charge but not atoms. This
complicates the actual calculations and the justification of extrapolation of the TB-LMTO parameters beyond the 5% range on either side of the equilibrium value is not valid.

A number of molecular dynamics studies of the geometrical and electronic structure of small clusters of various elements ([42, 43, 51]) have been performed. The ab-initio molecular dynamics (MD) approach developed by Car and Parinello [21] (CP) has been one of the most promising developments in this area. The method is based on the pseudopotential technique and therefore faces problems when dealing with the rather localized Delectrons of transition metals. Efficient soft pseudopotentials for transition metals are still not available and the CP generally is never applied to transition metal clusters.

Simple alkali metals clusters are fairly well described by the spherical jellium model. The quasi-free valence electrons occupy single-particle states in an effective spherically symmetric box potential. This is rather insensitive to the geometry of the atomic arrangement inside the cluster. Consequently one obtains a pronounced shell closing effect ([24]). Although the noble metals Cu, Ag and Au have closed d-shells and singly occupied outermost s-shell structures and several authors have suggested that there should be a close similarity to the shell closing effect in simple alkali metals, cohesive studies in the bulk metal and a series of EXAFS studies of Cu clusters supported on carbon ([8], [59]) indicate that the d-electrons through their hybridization with the s-electrons play an important role in the electronic structure and binding energy of these systems. [81] have also indicated through a series of experiments which include mass spectroscopy, oxygen and water absorption, that there is a competition of jellium-like electronic behaviour and icosahedral geometrical closure effects in small copper clusters.

In this chapter, we shall turn to the molecular version of the full-potential linearized muffin-tin orbital two-centre-fit (TCF) method suggested by [56] and [57] to carry out an ab initio study of Cu clusters ranging in size between 10 and 20.

2 The two-center fit method : TCF

The molecular version of the full potential-LMTO two-centre-fit (TCF) method utilizes the philosophy of Muffin-Tin Orbitals methods. It is based on the Density Functional Theory in the Local Density Approximation. The electron-electron interaction is treated approximately. In practice:

\[
\left[ -\nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})
\] (1)
where,
\[ \rho(r) = \sum_i f_i |\psi_i(r)|^2 \]

and,
\[ V_{\text{eff}} = V_N(r) + 2 \int \frac{\rho(r')}{|r - r'|} d^3r' + \mu_{xc}(\rho(r)) \]

The first step is the solution of the Schrödinger equation in a very *unpleasant* potential with Coulomb singularities. As in most approaches we use the variational approach. We choose a basis of representation \( \{ \phi_m(r) \} \) such that
\[ \Psi(r) = \sum_m c_m \phi_m(r) \]

The problem reduces to a matrix eigenvalue problem:
\[ \mathcal{H} = \varepsilon \mathcal{S} \]

Computation effort scales as \( \sim (\text{matrix dimension})^3 \). Our approach tries to use a minimal basis set at the expense of a rather complicated formulation. The basis is built up of Hankel functions \( H_{iL} \) diverging at \( r = R_i \), augmented inside the muffin-tin spheres by solutions \( u(r)Y_L(\hat{r}) \) of the Schrödinger equation:
\[ u''_L(r) = \left[ \frac{\ell(\ell + 1)}{r} + V(r) - \varepsilon \right] u_L(r) \]

with boundary conditions such that its logarithmic derivative matches that of the Hankel function. Any matrix element in this basis then can be written as:
\[ \langle \phi_{iL} | \mathcal{O} | \phi_{jL'} \rangle = \left[ \sum_k \int_{S_k} + \int_{I} \right] \phi^*_i L(r) \mathcal{O} \phi_{jL'}(r) d^3r \quad (2) \]

The Hankel functions associated with a muffin-tin at \( R_i \) can be written in terms of a Bessel function at \( R_j \) as \( \sum_{L''} S_{iL,kL''} J_{kL''} \), the structure matrix \( \mathcal{S} \) depends entirely on the geometric arrangement of the muffin-tins. The first integral becomes:
\[ = \sum_{k \neq i,j} \sum_{L''} S_{iL,kL''} S_{jL',kL''} \langle J_{L''} | \mathcal{O} | J_{L''} \rangle S_k + \sum_{k=i,j} S_{jL',iL} \langle H_L | \mathcal{O} | J_L \rangle S_i \ldots \]
\[ + \sum_{k=j,i} S_{iL,jL'} \langle J_L | \mathcal{O} | H_L \rangle S_j + \langle H_L | \mathcal{O} | H_L \rangle S_i \]
\[ = \mathcal{O}^{HH} + S^i \mathcal{O}^{JH} + \mathcal{O}^{HJ} \mathcal{S} + S^i \mathcal{O}^{JJ} \mathcal{S} \quad (3) \]
These are easy to calculate and there is a separation of atomic and structural information.

Most of the interstitial integral can be obtained from the muffin-tin spheres by using the fact that, in the interstitial, the basis are solutions of the Helmholtz equation, and using the Green theorem:

$$\int_I \phi_1^* \phi_2 d^3 \mathcal{L} = \frac{1}{\kappa_1^2 - \kappa_2^2} \sum_k \int_{S_k} [\phi_1^* \nabla \phi_2 - \phi_2 \nabla \phi_1^*] d^2 \mathcal{L}$$

$$\int_I \phi_1^* (-\nabla^2) \phi_2 d^3 \mathcal{L} = \kappa_2^2 \int_I \phi_1^* \phi_2 d^3 \mathcal{L}$$ (4)

If the potential here is a constant we can get by with the above. But for clusters this is definitely not so. In the molecular FPLMTO we use a tabulation technique.

We expand the product:

$$\phi_i^*(\mathcal{r}) \phi_j(\mathcal{r}) = \sum_m C_{ij}^m \chi_m(\mathcal{m})$$

where $\chi_m(\mathcal{r})$ is another set of muffin-tin centered H"ankel functions. In practice we put two atoms along the z-axis and make accurate numerical expansion by least squares fit for different distances and tabulate $C_{ij}^m(d)$:

$$A_{mn} = \int_I \chi_m^*(\mathcal{r}) \chi_n(\mathcal{r}) d^3 r$$

$$B_m = \int_I \phi_i^*(\mathcal{r}) \phi_j(\mathcal{r}) \chi_m(\mathcal{r}) d^3 \mathcal{L}$$

$$C = A^{-1} B$$

This is the two-centre fit table (TCF). For arbitrary geometry then we may easily calculate the necessary matrix elements by a fitting procedure to the table. The procedure is fast.

For molecular dynamics, the problem arises from the fact that the Pulay terms in the force are impossibly difficult to calculate directly as the basis set changes in a complicated manner when atoms move. To do the molecular dynamics, we use the Harris functional procedure as follows: At a time step $\tau_0$ we obtain the self-consistent charge density $\rho(r, \tau_0)$ using the FP-LMTO procedure. At a neighbouring time $\tau_0 + \tau$ we hazard a guess $\rho_g(r, \tau_0 + \tau)$ and obtain

$$\tilde{E}(\tau) = E_H[\rho_g(r, \tau_0 + \tau)]$$

$$= \sum_i \varepsilon_i [V_{eff}] - \int \rho_g(\mathcal{r}) V_{eff} [\rho_g(\mathcal{r})] + U [\rho_g(\mathcal{r})] + E_{xc} [\rho_g(\mathcal{r})]$$
To find the force on an atom, we simply move the atom with its surrounding charge density in a given direction. The force is given by

\[ \frac{\partial \tilde{E}}{\partial \tau} \bigg|_{\tau \to 0} \]

For dynamics we use the Verlet algorithm:

\[ r_{n+1} = 2r_n - r_{n-1} + \frac{E_m}{m} (\Delta t)^2 \]

where \( n \) denotes the time step of length \( \Delta t \). We can now either do straightforward molecular dynamics, but this often leads to unphysical heating/cooling of the system if our time steps are too large. For small time steps the procedure is inordinately slow. We add an extra friction term carefully \( F \Rightarrow F - \gamma m \dot{r} \). Methfessel and Schilfgaarde [56] have also used a free dynamics with feedback to overcome the above difficulty.

3 Results

We have chosen the various parameters for the FP-LMTO based on optimizing results for bulk Cu and the dimer. The values of \( \kappa^2 \) were chosen from optimum bulk calculations. The muffin tin radii were chosen as 1.9 Å to produce the bond length and binding energies of the Cu dimer correctly. For augmentation within the sphere we have used 4s, 4p, 3d, 4f and 5g functions (\( \ell_{\text{max}}=3 \)). For representation of interstitial functions we have used five \( \kappa^2 \) values with angular momentum cutoffs \( \ell_{\text{max}} = 4, 4.6, 2 \) and 1.

The optimum bond length was determined by varying the dimer bond length from 4.1 to 4.2 atomic units and calculating the total energy at each bond length. We found the optimum bond length to be 4.16 a.u with the binding energy (B.E) equal to 1.469 eV/atom. The table lists the various theoretical and experimental values for the bond length and binding energies per atom. It is well known that while the Hartree-Fock tends to under-bind, the LDA over-binds. Our bond lengths should then be smaller and binding energies larger than experimental values. This is borne out by the table. Clearly both the self interaction correction (SIC) and the gradient correction (GGA) improves matters. The TB-LMTO value of 0.23 eV/atom ([52]) is much too low and probably indicates serious lacunae in the treatment of clusters in that work rather than in the TB-LMTO itself.
Table 1: Bond lengths and Binding energies/atom for Cu$_2$ dimer

| Bond length (a.u.) | Binding Energy (eV/atom) | Method                  | Reference |
|--------------------|--------------------------|-------------------------|-----------|
| **Theoretical Results** |                          |                         |           |
| 4.55               | -                        | ab initio SCF           | [58]      |
| 4.28               | 0.923                    | LSD Pseudo.             | [79]      |
| 4.20               | 1.025                    | LSD Pseudo. + SIC       | [79]      |
| 4.28               | 0.975                    | LSD Pseudo. + CI        | [79]      |
| 4.56               | 0.34                     | Hartree-Fock            | [8]       |
| 4.55               | 1.04                     | CI                      | [8]       |
| 4.20               | 1.50                     | $X - \alpha$            | [8]       |
| 4.17               | 1.30                     | LCGO-DFT                | [14]      |
| 4.30               | 1.13                     | LCGO-GGA                | [19]      |
| 4.16               | 1.369                    | FP-LMTO-TCF             | Our work  |
| -                  | 0.23                     | TB-LMTO                 | [52]      |

| **Experimental Results** |                         |                         |           |
| 4.195               | 0.99                     | Expt                    | [10]      |
| 4.21                | 1.03                     | -                       | [9]       |
| -                   | 1.04                     | -                       | [58]      |
Table 2: Ionization potentials for \( \text{Cu}_2 \) by various methods

| IP (eV) | Method                        | Reference |
|---------|-------------------------------|-----------|
| 5.65    | \( \text{ab initio SCF } \Delta E \) | 58        |
| 6.04    | \( \text{ab initio SCF Koopman} \) | 58        |
| 7.987   | \( \text{LSD Pseudopotential} \) | 79        |
| 8.237   | \( \text{LSD Pseudopotential + SIC} \) | 79        |
| 6.37    | \( \text{Hartree-Fock} \) | 8         |
| 7.37    | \( \text{Modified Hartree-Fock-I} \) | 8         |
| 7.89    | \( \text{Modified Hartree-Fock-II} \) | 8         |
| 7.35    | \( X - \alpha \) | 8         |
| 7.64    | \( \text{EHT} \) | 8         |
| 5.70    | \( \text{LCAO-SCF} \) | 26        |
| 8.69    | \( \text{LCGO-DFT} \) | 19        |
| 7.904   | \( \text{LCGO-DFT + GGA} \) | 19        |
| 8.22    | \( \text{FP-LMTO-TCF} \) Our work |           |

The table shows the ionization potential (IP) for \( \text{Cu}_2 \) dimers, calculated as the difference between the total energies of neutral \( \text{Cu}_2 \) and the \( \text{Cu}^+ \) ion, using various methods. The experimental values quoted range between 7.904±0.04 quoted by Calamici et al \[19\] and 7.37 of Joyes and Leleyer \[47\]. It is quite clear that for the smaller clusters the generalized gradient corrections (GGA) to the local density approximation is very important \([19]\). Our FP-LMTO does not incorporate the GGA and hence leads to slightly larger values of the IP. The importance of self-interaction corrections (SIC) is not clear for dimers. Wang \[79\] includes SIC and obtains a higher value of the IP. Our work does not include the SIC.

The first test of the predictability of various methods first appear for \( \text{Cu}_3 \). The accompanying figure 1 shows the lowest energy structures predicted for the trimer. Miyoshi et al \[58\] find both the structures (O) and (A) to be almost degenerate in energy. The vertex angles are found to be 77.6° for (O) and 51.7° for (A). Calamici et al \[19\] find the structure (O) to be most stable with vertex angle 66.86° without SIC and 66.58° with SIC. The other structure (A) lies 0.023 eV higher in energy. Wang \[79\] finds the obtuse triangle shown on the right to be the stable structure. This has a vertex angle of 162°. He concludes that the SIC correction is essential and finds the acute triangle with a vertex angle of 47° to be the most stable. However, even with the SIC the structure quoted is rather different from other methods. Our
Table 3: Bond lengths, binding energies and ionization potentials of Cu$_3$

| Side length (a.u.) | Binding Energy (eV/atom) | IP (eV) | Reference |
|-------------------|--------------------------|--------|-----------|
| Theoretical Results |                          |        |           |
| 4.72              | 1.018                    | 4.39   | [58]      |
| 4.50              | 0.942                    | 7.144  | [79]      |
| 5.41              | 0.753                    | 6.018  | [79]      |
| 4.35              | -                        | 6.33   | [3]       |
| 4.28              | 1.34                     | 6.46   | [19]      |
| 4.45              | 1.12                     | 5.795  | [19]      |
| -                 | 0.68                     | -      | [52]      |
| 4.30              | 1.598                    | 6.40   | Our work  |
| Experimental Results |                        |        |           |
| -                 | 1.02                     | 5.48±0.5 | [80]     |

The prediction agrees reasonably well with the structure (O) of Miyoshi et al [58] and (O) of Calamici et al [19]. The vertex angle is 65° in our case. The isosceles shape is expected because of the possible Jahn-Teller distortion in Cu$_3$.

The table compares the bond lengths, binding energies and ionization energies of he Cu$_3$ trimer. We find the binding energy per atom to be 1.598 eV/atom which is higher than that for the linear configuration by 0.124 eV/atom. Over-binding because of the LDA is again observed. The ionization energy drops for the trimer and regains its value again for Cu$_4$. This has been observed in all the earlier works quoted and in experiment.

For N=4 we find the rhombus starting structure to lead to the most stable structure followed by the square and the tetrahedron in decreasing order of stability. Our prediction matches exactly with that of Akeby et al [2] and Calamici et al [19] who also predicted the sequence rhombus, square and tetrahedron. The larger rhombus angle turns out to be 120° which agrees well with the prediction of 122° by Calamici et al [19]. Our ionization potential is 7.90 eV, which agrees not badly with 7.0±0.6 eV found experimentally. The TB-LMTO ([52]) predicts the order of stability to be the tetrahedron, the rhombus and the square in decreasing stability. This does not match with any other work and possibly has its origin in the problem talked about earlier.

For Cu$_5$ we find the trigonal bipyramid with B.E. 2.187 eV/atom to be the
most stable structure followed by the square pyramid where the difference in B.E. between the two structures is .056 eV only. Akeby et al [2] also obtain the trigonal bipyramid to be more stable than the square pyramid agreeing with our calculations. Calamici et al [19] finds another structure, the flat pentagonal trapezoid to be almost degenerate; actually 0.009 eV lower in energy than the trigonal bipyramid. They find the square pyramid to be more than 0.309 eV higher in energy. We would like to emphasize with Calamici et al that for the smaller clusters the GGA may play a crucial role in stabilizing certain structures.

Figure 3 shows the variation of the ionization potential with cluster size. The troughs at n=3 and n=5 agree well with earlier works as well as experimental results ([50]).

For N=6 we have considered two starting structures the square bipyramid (octahedron) and the capped trigonal bipyramid which is obtained by capping one face of the trigonal bipyramid so that the capping atom is equidistant from all the three atoms on the face. We find the capped trigonal bipyramid to be the most stable structure with bond energy equal to 2.405 eV/atom which is 0.040 eV/atom higher than the square bipyramid (octahedron). The TB-LMTO calculations predict the octahedron to be the most stable structure compared to other random structures. Also the numerical value of 1.56 eV/atom for the octahedron obtained from the TB-LMTO calculations is much lower compared to our value.

The pentagonal bipyramid, the capped square bipyramid and the bicapped trigonal bipyramid were considered as the starting structures for our calculations for N=7. We find the pentagonal bipyramid to be the most stable structure in accordace with Akeby et al. but at variance with the TB-LMTO results. The bicapped trigonal bipyramid is slightly higher in energy (0.002 eV/atom) than the capped square pyramid in our calculations.

For Cu₈ we considered three starting structures as shown in the table of which the capped pentagonal bipyramid turns out to be the most stable followed by the bicapped square bipyramid and the cube. TB-LMTO predicts the antiprism followed by the bi-tent structure and the cube. Both the methods find the cube to b ethe least stable though our B.E. for the cube is 0.592 eV/atom higher than the TB-LMTO results.

In the case of Cu₉, we considered the tricapped square bipyramid and the bicapped pentagonal bipyramid with the capping atoms on adjacent and non-adjacent faces. The tricapped square bipyramid was found to be the most stable structure followed by the bicapped pentagonal bipyramid with the capping atoms on adjacent faces (lower by only 0.006 eV/atom) and the bicapped pentagonal bipyramid (non-adjacent faces) lower by 0.025 eV/atom than the most stable structure in this
range. The stable shapes for $6 \leq N \leq 9$ are shown in figures 4.

Figure 5 shows a plot of the binding energy versus cluster size for $N=2$ to 9. The relative stability of the clusters $(2E(N) - E(N+1) - E(N-1))$ is also plotted on the same graph. Cluster sizes $N=3,5$ and 8 show up as more stable. This has been predicted experimentally earlier by Knickelbein [50]. Katakuse [48] has also observed $N=8$ to be a stable structure in their experimental observations.

Figure 6 shows a plot for the HOMO-LUMO gap versus cluster size for the most stable clusters. In the theoretical results of Akeby et al [2] the HOMO-LUMO gap for the $Cu_8$ cluster is determined to be 1.93 eV while Lammers and Borstal [52] report a value of 1.91 eV. Our calculated value for the HOMO-LUMO gap for the most stable structure (capped pentagonal bipyramid) is 1.156 which is lower than both the reported values. The HOMO-LUMO gap does show a peak at $N=8$ in our calculations but we cannot conclude from this point that this is a manifestation of shell closure. We also see a minimum in the HOMO-LUMO gap value at $N=6$ unlike in [52]. Moreover pronounced odd-even alterations in the HOMO-LUMO gap values as predicted by the shell model [75] are not recognizable in our calculations.

The $N=10$ cluster shape is a close competition between the tetracapped trigonal bipyramid which is obtained by capping the $N=9$ cluster on another face and the structure shown on the right hand side of figure 6. Our calculations indicate that the former is more stable, however, the energy difference is smaller than the errors involved in the FP-LMTO itself. From $N=11$ to $N=13$ the clusters grow towards the stable icosahedron. These shapes indicate that probably our prediction is valid.

For $N=12$ we started from a configuration which is an icosahedron with a void at the centre. Rapidly the structure evolved to the icosahedron with one exterior atom removed.

For $N=13$ we studied carefully two possible structures: the cubo-octahedron (shown in the left in figure 9 and the icosahedron, shown on the right of the same figure. Our calculations indicate that even if we begin with the cubo-octahedron as our starting structures, the cluster rapidly settles down to the icosahedron. Earlier Valkealahti and Manninen [78] had also used effective medium-molecular dynamics and shown that the cubo-octahedron is unstable and rapidly changes over to the stable icosahedron. Winter et al [81] have argued from experimental observations that the shell structure seen in the smaller clusters is overshadowed by icosahedral closures from $N=13$ onwards.

For $N=15$ and $N=16$ we see near-degenerate structures. The lower-energy structure has atoms on neighboring faces of the icosahedron. There is also another structure, differing in energy by about 1%, in which the “extra” atoms are on non-neighboring faces of the icosahedron. For $N=17$ the two different starting
structures both anneal to an icosahedron with four atoms on neighboring faces.

The $N = 19$ has a very stable structure: the double icosahedron, further confirming the conjecture of Winter et al. \[81\] regarding icosahedral closure. For $N = 20$ The equatorial addition was found to be more stable by about 1%. We expect as the size increases, the cluster structure becomes more spherical. Note that we see no evidence for the very open structure reported to have been obtained by Lammers and Borstal \[52\] for $N = 20$ through simulated annealing.

Figure 12 shows the binding energy and the homo-lumo gap for the clusters $N = 11$ to $N = 20$. We note that the signatures of shell closure we observed in the smaller clusters is overtaken by geometric closures and the icosahedron based closed structures are the more stable.

Acknowledgements

We should like to thank Profs. M. Methfessel and M. Van Schilfgaarde for making the entire mechanism of the FP-LMTO available to us and enthusing us to make use of this powerful technique.

References

[1] Adachi H, Tsukada M abd Satoko C 1978 J. Phys. Soc. Japan 45 875
[2] Akeby H., Panas I., Pettersson L.G.M., Siegbahn P. and Wahlgren U., J. Phys. Chem. 94 5471 (1990).
[3] Amos A T, Brook P A and Moir S A 1988 J. Phys. Chem. 92 733
[4] Anderson A B and Hoffman R 1974 J. Chem. Phys. 61 4545
[5] Anderson A B 1977 J. Am. Chem. Soc. 99 696
[6] Anderson A B 1977 J. Chem. Phys. 66 5108
[7] Anderson A B 1978 J. Chem. Phys. 68 1744
[8] Apai G., Hamilton J.F., Stohr J. and Thompson A., Phys. Rev. Lett. 43 165 (1979).
[9] Aslund N, Barrow R F, Richards W G and Travis D N 1965 Ark. Fys. 30 171
[10] Bachmann C, Demuynck J and Veillard A 1978 Gazz. Chim. Ital. 108
[11] Baetzold R C 1971 J. Chem. Phys. 55 4363
[12] Baetzold R C and Mack R E 1975 *J. Chem. Phys.* 62 1513
[13] Baetzold R C 1978 *J. Phys. Chem.* 82 738
[14] Bagus P S and Seel M 1981 *Phys. Rev.* B23 2065
[15] Basch H., Newton M D and Moscowitz J W 1980 *J. Chem. Phys.* 73 4492
[16] Balerna A., Bernicri E., Piccozi P., Reale A., Santucci S., Burrattini E. and Mobilio S., *Surf. Sci.* 156 206 (1985).
[17] Blyholder G 1974 *Surf. Sci.* 42 249
[18] Busby R., Koltzbücher W and Ozin G A 1976 *J. Am. Chem. Soc.* 98 4013
[19] Calamici P, Köster A M, Russo N and Salahub D R 1996 *J. Chem. Phys.* 105 9546
[20] Callear A B and Conner J, 1972 *Chem. Phys. Lett.* 13 245
[21] Car R. and Parinello M., *Phys. Rev. Lett.* 55 2471 (1985).
[22] Castro M and Salahub D R 1993 *Phys. Rev.* B47 10955 ; 1994 *Phys. Rev.* B49 11842
[23] Christensen O B, Jacobsen K W, Nørskov J K and Manninen M 1991 *Phys. Rev. Lett.* 66 2219
[24] Cleveland C L and Landman U 1991 *J. Chem. Phys.* 94 7376
[25] Conrad H, Ertl E., Königinger H, Küppers J and Latta E E 1976 *Chem. Phys. Lett.* 42 115
[26] Cox P, Bénard M and Veillard A 1982 *Chem. Phys. Lett.* 87 159
[27] Datta A., Mookerjee A. and Bhattacharyya A.K., 1994 *Mod. Phys. Lett.* B8 883
[28] Datta R.P., Banerjea A., Mookerjee A. and Bhattacharyya A.K., 1996 *Mod. Phys. Lett.* B10 211
[29] Datta R.P., Banerjea A, Mookerjee A and Bhattacharya A.K, 1997 *Int. J. Mod. Phys.* B11 255
[30] Demuynck J, Rohmer M -M, Strich A and Veillard A 1981 *J. Chem. Phys.* 75 3443
[31] Devore T C, Ewing A, Franzen H F and Calder V, 1975 *Chem. Phys. Lett.* 35 78
[32] Fan L and Ziegler T 1991 *J. Chem. Phys.* 95 7401
[33] Fournier R, Andzelm J and Salahub D R 1989 *J. Chem. Phys.* 90 6371
[34] Gates B C and Lieto J 1980 *CHEMTECH* (Amsterdam) 10 195 ; 248
[35] Good B S and Banerjea A 1992 *Mat.Res.Soc. Symp. Proc.* 278, 211 (1992)
[36] Goodwin L and Salahub D R 1993 *Phys. Rev.* A47 774
[37] Häkkinen H and Manninen M 1989 *J. Phys.: Condens. Matter* 1 271
[38] Huber H, Kündig E P, Moscovitz M and Ozin G A 1975 *J. Am. Chem. Soc.* 97 2097
[39] Huber H, Ozin G A and Power W J 1975 *J. Am. Chem. Spec.* 98 6508
[40] Huber K.P and Herzberg G., *Constants of Diatomic molecules, Molecular Spectra and Molecular Structure Vol.IV* (Van Nostrand, Princeton, 1979).
[41] Hulse J E and Moscovitz M 1977 *J. Chem. Phys.* 66 3988
[42] *Proceedings of the Fourth International Meeting on Small Particles and Inorganic Clusters*, Marseilles, France (1988), published in *Z.Phys.* D12
[43] *Fifth International Meeting on Small Particles and Inorganic Clusters*, Konstanz, Germany (1991), published in *Z.Phys.* D19 and D20
[44] Jacobsen K W, Nørskov J K and Manninen M 1987 *Phys. Rev. Lett.* 66 2219
[45] *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, Vol. 1 and 2, Eds. Jena P, Khanna S N and Rao B K 1992 (Kluwer Academic Publishers, Netherlands 1992)
[46] Jerrard R J, Amos A T and Brook P A 1982 *Theor. Chim. Acta* 61 163
[47] Joyes P and Leleyer M, 1973 *J. Phys. B: At. Mol. Phys.* 6 150
[48] Katakuse I, 1986 *Int. J. Mass. Spectrom. Ion Phys.* 74, 33
[49] Katsuki S and Taketa H 1981 *J. Phys. Soc. Japan* 50 855
[50] Knickelbein M B 1992 *Chem. Phys. Lett.* 192 129
[51] *Clusters and Fullerenes*, Eds. Kumar Vijay, Martin T P and Tosatti E (World Scientific 1993)
[52] Lammers U. and Borstel G., 1994 *Phys. Rev.* B 49 17360
[53] Lauher J W 1979 *J. Am. Chem. Soc.* 101 2604
[54] Messmer R P, Knudson S K, Johnson K H, Dismond J B and Yang C Y 1976 *Phys. Rev.* B13 1396
[55] Messmer R P, Salahub D R, Johnson K H and Yang C Y 1977 Chem. Phys. Lett. 51 84

[56] Methfessel M.S. and van Schilfgaarde M., 1993 Phys. Rev. B48 4937 ; 1993 Int. J. Mod. Phys. B7 262

[57] Methfessel M.S., Schilfgaarde M. and Schaffler M., 1993 Phys. Rev. Lett. 70 29

[58] Miyoshi E, Tatedwaki H and Nakamura T 1983 J. Chem. Phys. 78 815

[59] Montano P.A., Purdum H., Shenoy G.K., Morrison T.I. and Schultze W., Surf. Sci. 156 216 (1985).

[60] Moscovitz M and Hulse J E 1977 J. Chem. Phys. 67 4271

[61] Noell J O, Hay P J, Martin R L and Bobrowicz F W 1980 J. Chem. Phys. 73 2360

[62] Ozin G A 1976 Appt. Spectroscopy30 573

[63] Ozin G A, Huber H, McIntosh D, Mitchell S, Norman jr J G, Noodleman L 1979 J. Am. Chem. Soc. 101 3504

[64] Ozin G A 1977 Catal. Rev. 16 191

[65] Pelissier M 1981 J. Chem. Phys. 75 775

[66] Post D and Baerends J 1982 Chem. Phys. Lett. 86 176

[67] Raoult B, Farges J, De Feraudy M F and Torchet G 1989 Z. Phys. D 12 85

[68] Rohlfing E A and Valentini J J 1986 J. Chem. Phys. 84 6560

[69] St-Amant A and Salahub D R 1990 Chem. Phys. Lett. 169 387

[70] Schmeisser D S, Jacobi K and Kolb D M 1981 J. Chem. Phys. 75 5300

[71] Sim F, Salahub D R, Chin S and Dupuis M 1991 J. Chem. Phys. 95 4317

[72] Smith J R and Banerjea A 1987 Phys. Rev. Lett. 59 2451

[73] Smith J R and Banerjea A 1988 Phys. Rev. B37 10411

[74] Smith J R, Perry T and Banerjea A 1991 Phys. Rev. B44 6444

[75] Sugano S, Microcluster Physics, Springer series in Mat. Sc. Vol. 20 (Springer Verlag, Berlin, Heidelberg, 1991).

[76] Tatewaki H, Miyoshi E and Nakamura T 1982 J. Phys. Chem. 76 5073

[77] Upton T H and Goddard W A III 1978 J. Am. Chem. Soc. 100 5659 389 ; 1980 Faraday Symp. Chem. Soc. 14 170
[78] Valkealahti S and Manninen M 1992 *Phys. Rev.* 45 9459
[79] Wang S 1985 *J. Chem. Phys.* 82 4633
[80] Weltner W and van Zee R J 1984 *Ann. Rev. Phys. Chem.* 35 291
[81] Winter B J, Parks E K and Riley S J 1991 *J. Chem. Phys.* 94 8618
FIGURE CAPTIONS

1 Various shape predictions for the Cu₃ trimer
2 Stable configurations for Cu₄ and Cu₅
3 Variation of the ionization potential with cluster size
4 Stable configurations for Cu₆ to Cu₉
5 The binding energy per atom and its curvature for Cu₂ to Cu₉
6 The homo-lumo gap for Cu₂ to Cu₉
7 The structures for Cu₁₀
8 The stable structures for Cu₁₁ and Cu₁₂
9 The structures for Cu₁₃
10 The structures for Cu₁₄ – Cu₁₈
11 The structures for Cu₁₉ – Cu₂₀
12 The binding energy per atom and the homo-lumo gap for Cu₁₁ to Cu₂₀
Miyoshi et.al.

Calaminici et.al.

Wang

Our Work

LSDF+SIC

LSDF

Wang

Calaminici et.al.

Miyoshi et.al.
