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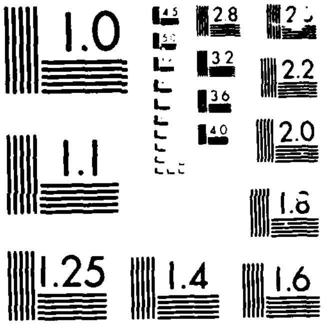
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SPHERICAL CLUSTERS OF SIMPLE METALS: MADELUNG ENERGIES AND STRUCTURE

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SPHERICAL CLUSTERS OF SIMPLE METALS: MADELUNG ENERGIES AND STRUCTURES

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The Madelung energies of simple metal spheres are calculated for bcc, fcc, and hcp structures as well as for fully relaxed structures. It is found that for clusters of up to 40 atoms the structure generally does not have the symmetry of any simple lattice. The variation of the structural part of the total energy is shown to be slightly smaller than the variation arising from the filling of discrete single-electron energy levels.

Recent experiments[1,2] on the 'magic numbers' of small sodium clusters suggest that variation of the binding energy of clusters as a function of their size is dominated by the filling of energy levels of electrons moving in a spherical potential[3]. This simple interpretation is supported also by good agreement of the calculated electronic polarizabilities[4] with the experimentally measured ones[5]. *Ab initio* calculations[6,7] of the structures of the clusters have been performed only for the smallest clusters. These give the striking result that for up to six atoms the ground-state structure of the cluster is planar. However, these nonspherical structures are *not* entirely in contradiction with the spherical jellium picture, since the structures can be well understood by studying the single electron wave functions in a spherical potential: in the case of a partly filled shell the charge density will be nonspherical and the total electrostatic energy can be reduced by relaxing the ions to a configuration which has the shape of the electron density distribution.

For large clusters it is expected that the electron density distribution starts to be more and more spherical as the cluster increases. It is then appealing to make a spherical approximation in determining the cluster structures. Recently, Iñiguez et al[8] have used this approximation and the density functional scheme to calculate the binding energies of sodium clusters in some bcc and fcc configurations. A related calculation was published earlier by Buttet et al[9]. The results show large variations in the cluster binding energy as a function of the cluster size, and Iñigues et al[8] conclude that the actual clusters have "disordered" structures which are more spherical than those that can be formed from simple bcc and fcc lattices.

The purpose of this communication is to show that if the electron density distribution is assumed to be spherically symmetric, the resulting ionic configuration is determined mainly due a classical Madelung energy. Furthermore it is shown that the ground state structures of the clusters are generally not small pieces of simple lattices (bcc, fcc, or hcp), but take always a more spherical shape (e.g. icosahedral in the case of a 13 atom cluster). The variation of the structural energy as a function of the cluster size is found to be somewhat smaller than the variation arising from the filling of single electron energy shells giving support to the idea that the dominant magic numbers are determined by the electronic shell structure of a square well potential.

In the density functional method, the total energy of the cluster is written as[8]

$$E_T = T[n] + E_{xc}[n] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+ \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} + \sum_i\int d\mathbf{r}V_{ps}(\mathbf{r}-\mathbf{R}_i)n(\mathbf{r}), \qquad (1)$$

where T and E_{xc} are the kinetic and exchange-correlation energies, $n(\mathbf{r})$ is the electron density, $\mathbf{R}_i$ the ion site, and V_{ps} the electron-ion pseudopotential. Now we define a fictitious charge density distribution n_0 as a step function

$$n_0(r) = n_0\theta(R_c-r), \qquad (2)$$

where R_c is the cluster radius, and n_0 is the average conduction electron density in an infinite metal. $n_0(r)$ is equal to the compensating positive background density in a jellium cluster. By adding and subtracting electrostatic energy terms in Eq. (1) we can write the total energy as

$$E_T = T[n] + E_{xc}[n] + E_M$$
$$+ \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')-n_0(\mathbf{r})n_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+ \sum_i\int d\mathbf{r}V_{ps}(\mathbf{r}-\mathbf{R}_i)n(\mathbf{r}) + \sum_i\int d\mathbf{r}\frac{n_0(r)}{|\mathbf{r}-\mathbf{R}_i|}, \qquad (3)$$

where the Madelung energy E_M is defined as

$$E_M = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n_0(r)n_0(r')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+ \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} - \sum_i\int d\mathbf{r}\frac{n_0(r)}{|\mathbf{r}-\mathbf{R}_i|}. \qquad (4)$$

The advantage in writing the total energy in this form is that most of the structural dependence of the energy is included in the Madelung energy. This is analogous to the classical cleavage energy in calculating the surface energy in the same method[10]. The two last terms in Eq. (3) also depend explicitly on the structure. Using for example a Heine-Abarenkov[11] or Ashcroft[12] type pseudopotential which equals the $1/r$ potential beyond a core radius, say r_c, it is easy the see that the structure dependent parts of the two last terms in Eq. (3) roughly cancel each other. These two terms can be written as

$$\sum_i \int d\mathbf{r} V_{ps}(\mathbf{r}-\mathbf{R}_i)[n(\mathbf{r})-n_0(\mathbf{r})]$$

$$+\sum_i \int_{|\mathbf{r}-\mathbf{R}_i|<r_c} d\mathbf{r} \left[V_{ps}(\mathbf{r}-\mathbf{R}_i)n_0(\mathbf{r}) + \frac{n_0(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|} \right]. \qquad (5)$$

The structural dependence of the first term comes only due to the difference $n-n_0$ which is markedly nonzero only in a narrow region at the surface. The structural dependence of the second term is also small since the integral is limited only over the core regions of the pseudopotentials. Since the other terms of Eq. (3) also depend only weakly on the structure[13] it is reasonable to assume that only the Madelung energy depends strongly on the structure. Thus in determining the *structure* of the clusters, the calculation of the electronic structure is not needed at all (note that all this is based on the assumption that the resulting electron density distribution as a result of a self-consistent density functional calculation is spherical). This fact, that the structural dependence of the total energy is dominated by the Madelung energy, has been noticed earlier in calculating surface energies[14–16] and void formation energies[16] in simple metals.

We have calculated the Madelung energies of clusters up to 40 atoms. The cluster structures considered are bcc, fcc, and hcp lattice structures and the fully relaxed structure which minimizes the Madelung energy. The results for the binding energy (i.e. negative of the Madelung energy) is shown in Fig. 1. The relaxed ground state always has a much higher binding energy than any simple lattice configuration. In calculating the Madelung energies of bcc, fcc, and hcp clusters the lattice constant was fixed to correspond to the electron density n_0. The calculations were repeated for all three lattices by taking the center of the cluster to be a lattice site, tetrahedral interstitial site, octahedral interstitial site, midpoint of two nearest atoms, or the center of a equilateral triangle of three closest atoms. The optimal *lattice* structures (bcc, fcc, or hcp) for clusters from 1 to 40 atoms are given in Table 1. These structures are generally very different from the actual ground state structures, which were obtained by letting the ions relax to positions which minimize the Madelung energy. Some of these structures are shown in Fig. 2. Many of these also have a high symmetry, but different from any simple lattice symmetry. Generally, up to the size of 12 atom cluster, all the atoms are evenly distributed on a shell having roughly the same distance from the center of the cluster (there is no atom in the center of the cluster). The 13 atom cluster is an icosahedron with an atom in the center, but again in the 14 atom cluster all the atoms are on one shell, the center being empty. From 15 to 21 atom clusters there is one atom in the center and the rest of the atoms are evenly distributed on the surface, nearly the same distance from the center. Larger clusters start to have more atoms also inside the cluster, but the surface always seems to take as spherical a shape as possible.

From Figure 1 it is obvious that for only a few cluster sizes does the lattice structure come even close to the binding energy of the fully relaxed optimal configuration. The large variation as a function of the cluster size disappears almost totally when the ions are allowed to relax from the lattice sites to the optimal ground state configuration. The remaining variation is slightly smaller than the variation of the purely electronic part of the energy in the jellium model[17] (coming essentially from the first three terms of Eq. (2)). This is clearly seen in Fig. 3 where the second derivative of the energy versus cluster size curve is shown for the Madelung energy and for the energy of the jellium model. This result has the important consequence that even if the actual interactions between the electrons and the ions are taken into account, magic numbers may still be determined by the filling of the single particle energy levels in a spherical potential. The results of surface energy calculations in a related model show that the structure dependence will be reduced if the electron density is allowed to relax from the jellium result[14]. It is then expected that the variation of the structural part of the energy is overestimated if only the Madelung energy is considered. The noncrystalline cluster structures seem to persist up to cluster sizes of several hundreds of atoms. This is indicated by the results of Iñigues et al[8] which show that the binding energies of the crystalline structures remain lower than those of the optimal structures even at cluster sizes of more than 90 atoms. Also the calculations of the reconstruction of simple metal surfaces[18] indicate that the registration shift extends several layers below the surface and originates from the same electrostatic forces as the noncrystalline cluster structures. (The cluster size has to be larger than about 500 atoms before more than half of the atoms are not in the surface layer). For very large clusters, of course, the strictly spherical shape will be modified by faceting which will eventually make the crystalline structure more stable than the (disordered) spherical one.

In conclusion, we have shown that the main part of the structural dependence of the total energy of small simple metal clusters comes from the classical Madelung energy. The calculations for ground state structures show that this Madelung energy varies as a function of the cluster size less than the electronic contribution which shows the shell structure. This result gives further understanding why the magic numbers can be understood in terms of a spherical jellium model, and predicts that cluster structures differ from crystalline structures up to cluster sizes of hundreds of atoms.

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FIGURE CAPTIONS

Fig. 1. Calculated Madelung energies as a function of the cluster size. The upper curve shows the results for the fully relaxed structures and the lower curve is the result for the most stable bcc, fcc or hcp structures. The Madelung energy for the bulk bcc and fcc lattices is also shown in the figure. E_M is given in atomic units for a density, n_0, corresponding to r_s=1.

Fig. 2. Examples of cluster structures determined by minimizing the Madelung energy.

Fig. 3. The variation of the Madelung energy (in atomic units) as a function of the cluster size (a) as compared to the variation of the total energy of the jellium model[17] (b). The results are for lithium (r_s=3.25).

Table 1. Optimal structures of spherical clusters assuming them to have bcc, fcc, or hcp structures. The center of the cluster has been chosen to be lattice site (lat), midpoint of two atoms (mid), tetrahedral interstitial site (tet), octahedral interstitial site (oct), or the center of an equilateral triangle (tri).

Size	Lattice(center)	Size	Lattice(center)
1	-	21	hcp(tet)
2	bcc(mid)	22	hcp(tet)
3	fcc(tri)	23	hcp(mid)
4	fcc(tet)	24	hcp(tet)
5	fcc(oct)	25	hcp(tri)
6	fcc(oct)	26	hcp(tri)
7	fcc(oct)	27	hcp(tri)
8	fcc(oct)	28	hcp(tet)
9	fcc(oct)	29	hcp(tet)
10	hcp(mid)	30	hcp(tet)
11	bcc(lat)	31	bcc(tet)
12	fcc(lat)	32	hcp(tet)
13	fcc(lat)	33	hcp(oct)
14	bcc(lat)	34	bcc(mid)
15	bcc(lat)	35	hcp(oct)
16	bcc(lat)	36	fcc(oct)
17	hcp(lat)	37	fcc(oct)
18	bcc(lat)	38	fcc(oct)
19	fcc(lat)	39	fcc(oct)
20	hcp(tet)	40	fcc(oct)

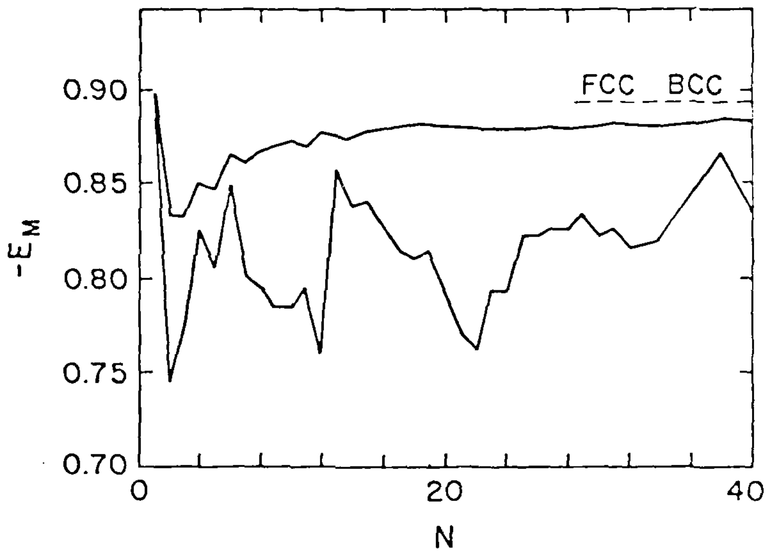
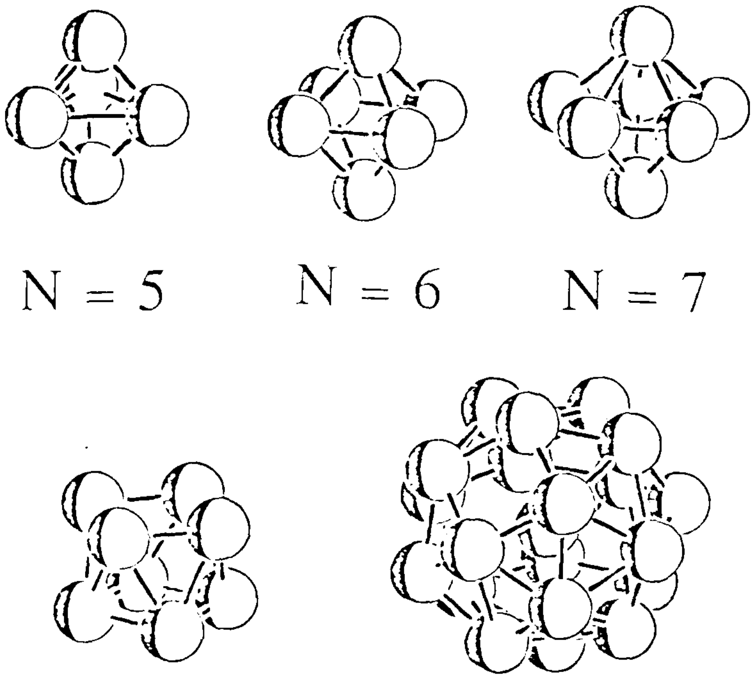


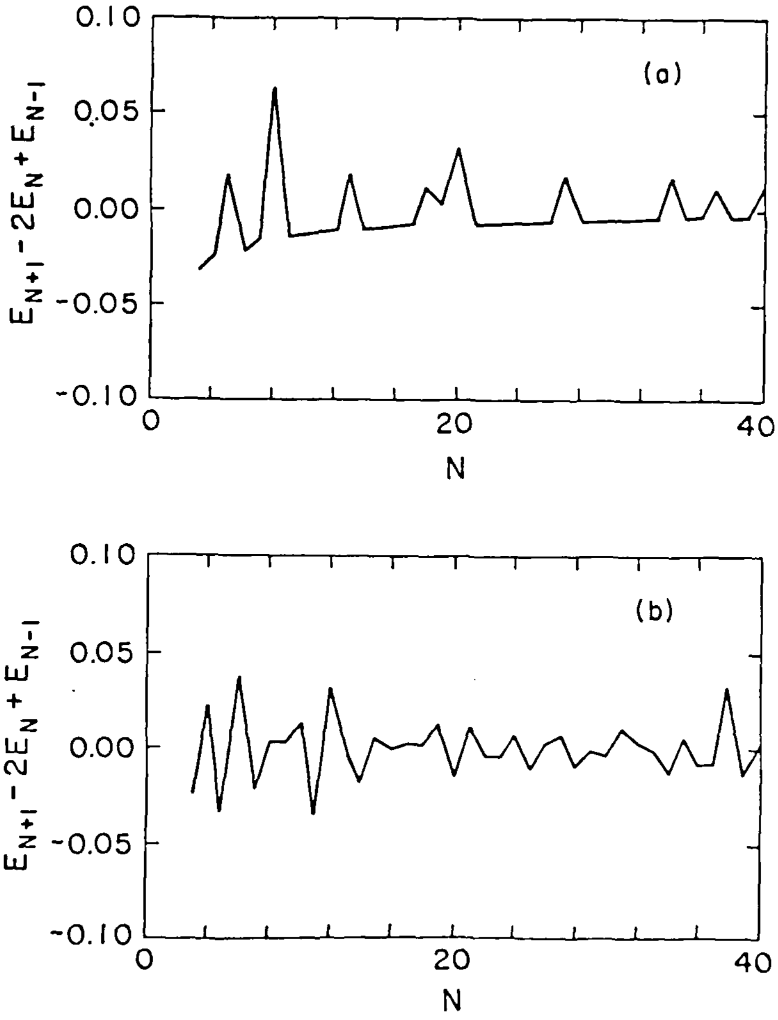
Figure 1



$N = 5$ $N = 6$ $N = 7$

$N = 8$ $N = 21$

Figure 2.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0.05
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-0.05
-0.10
0
20
40
N
$E_{N+1} - 2E_N + E_{N-1}$
(a)
0.10
0.05
0.00
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-0.10
0
20
40
N
$E_{N+1} - 2E_N + E_{N-1}$
(b)

Figure 3.

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