The Periodic System of Metal Clusters – a Tool for Deriving Various Forms of »Cluster-Matter«

Hans Müller and Christian Opitz

*Institut für Physikalische Chemie der Friedrich-Schiller-Universität Jena,
Am Steiger 3, Haus 3, D-07743 Jena*

A simple modified jellium model permits calculation of all the magic numbers of large metal clusters M_N up to $N = 1432$ in excellent agreement with experimental data. This success justifies further conclusions to be drawn from this model: (1) the calculated aufbau principle enables construction of a Periodic System of (alkali metal) Clusters (PSC); (II) this PSC, strictly speaking a Periodic System of »giant atoms«, is a powerful tool for predicting the reactivity of free electron-like metal clusters; (III) the formation of cluster dimers is discussed exemplarily in detail in excellent agreement with experimental and theoretical experience; (IV) various forms of cluster-matter are outlined in relation to new materials; (V) a great deal of work has to be done to confirm a number of unconventional predictions: new experiments and new calculations are highly desirable.

INTRODUCTION

In the early thirties, nuclear physicists applied a number of »auxiliary potentials«: spherical well (infinite walls, Gamow,[1] finite walls, Margenau[2]) and spherical oscillator (Heisenberg[3]) which introduce various shell models to explain the magic numbers MN of stability for atomic nuclei.[4]

Similar models have been used in the literature to successfully describe shell structure in metal clusters.[5–13]

Very recent experimental results for various metal clusters, particularly those of alkali metals[14–18] and of metals from the third main group of the Periodic Table[19–21] give considerable evidence for shell structure in the electronic states up to about 1500 electrons.

Using these similarities in the shell structure calculation of atomic clusters and nuclei and developing more sophisticated potential models,[22] we are able to calculate not only correct magic numbers MN of metal cluster stability but also proper bunching of subshells[23] in excellent agreement with all the measured MN of large alkali metal clusters up to 1500 atoms[14-18] (*cf.* Figure 1).

Even a tentative application of our model to clusters Al_N and Ga_N[19-21] shows amazingly good results.

On the basis of this success, we are encouraged to check further information from our model.[24]

In the first section, we develop a Periodic System of (alkali metal) Clusters (PSC) using the calculated aufbau principle and compare this PSC with the wellknown Periodic System of Elements (PSE). The projection of the first eight main groups from the PSC generates a nice »Periodic Systems of Giant Atoms«.[25]

Next, we demonstrate how to predict the »chemistry of free electron-like metal clusters« from PSC. This gives us an interesting opportunity to speculate on various forms of »cluster-matter« like »cluster-molecules«, »cluster-crystals«, and »cluster-metals«, respectively, which may be applicable to new material designs.[26]

In this paper, we discuss cluster-molecules or, more strictly speaking, the formation of cluster-dimers (homonuclear and heteronuclear giant diatomics) in more detail. We start by checking many unconventional predictions.

A PERIODIC SYSTEM OF (ALKALI METAL) CLUSTERS (PSC)

We have used the aufbau principle generated from a modified analytic sphere model

$$1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 1g^{18} 2d^{10} 1h^{22} 3s^2 2f^{14} 1i^{26} 3p^6 2g^{18} 1j^{30} 3d^{10} 4s^2$$
$$2h^{22} 1k^{34} 3f^{14} 1l^{38} 2i^{26} 4p^6 3g^{18} 1m^{42} 2j^{30} 4d^{10} 5s^2 3h^{22} 1n^{46} 2k^{34} 4f^{14} 5p^6 \qquad (1)$$
$$1o^{50} 3i^{26} 2l^{38} 4g^{18} 1q^{54} 5d^{10} 3j^{30} 2m^{42} 6s^2 4h^{22} 1r^{58} 3k^{34} 2n^{46} 5f^{14} 6p^6 1t^{62}$$
$$4i^{26} 2o^{50} 3l^{38} 5g^{18} 6d^{10} 7s^2 1u^{66} 4j^{30} 2q^{54} 3m^{42} 5h^{22} 1v^{70} \ldots$$

(*cf.* Figure 1) in order to construct a Periodic System of (alkali metal) Clusters (PSC).

The number and structure of the main groups of both the Periodic System of (alkali metal) Clusters (PSC) and Periodic System of Elements (PSE) are defined by the four deepest states of the aufbau principle only (*cf.* Figure 2).

The fine structure of the open PSC exhibits 18 main groups (s-, p-, d-clusters) and an infinite number of subgroups (f-, g-, h-, ... clusters) (*cf.* Figure 3).
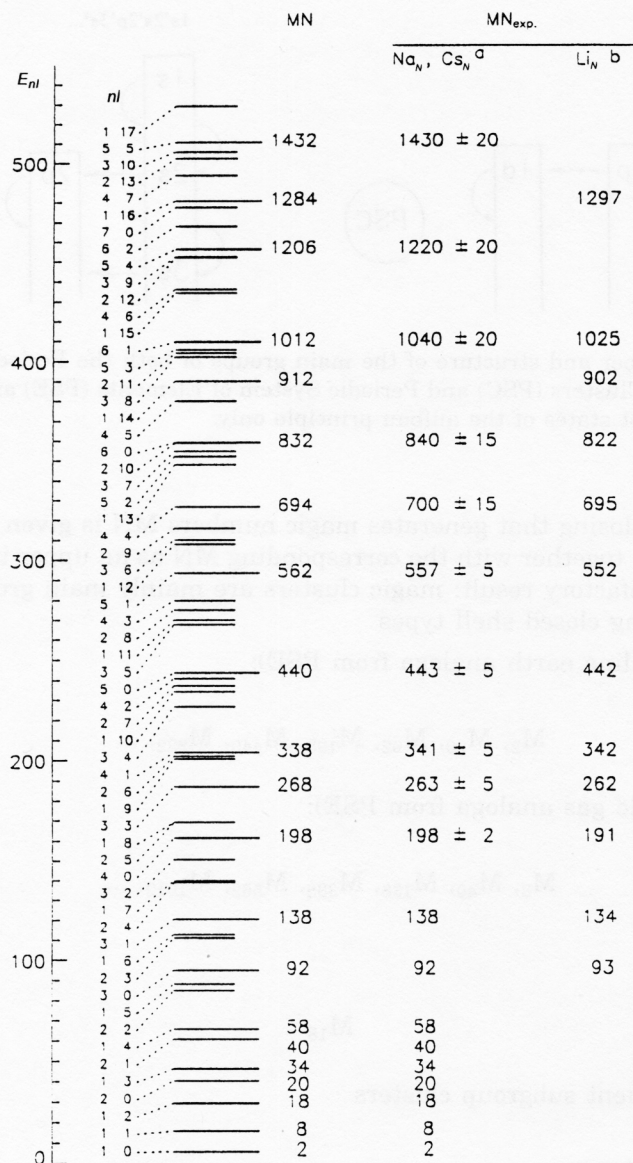
Figure 1. One-electron jellium states $E = E_{nl}/(\hbar^2/2mR^2)$ of a 1500 electron alkali metal cluster M_{1500} calculated by using an optimized piecewise constant perturbation including calculated (MN) and measured magic numbers (MN$_{exp}$; (a[14–17], b[18]). Our energy unit depends on particle size N and on alkali metal M (cf. Eq. (3)). As a result, the drawn shell structure is valid independently of cluster size for all alkali metal clusters. This »universal« shell structure makes it is easier to draw more general results.
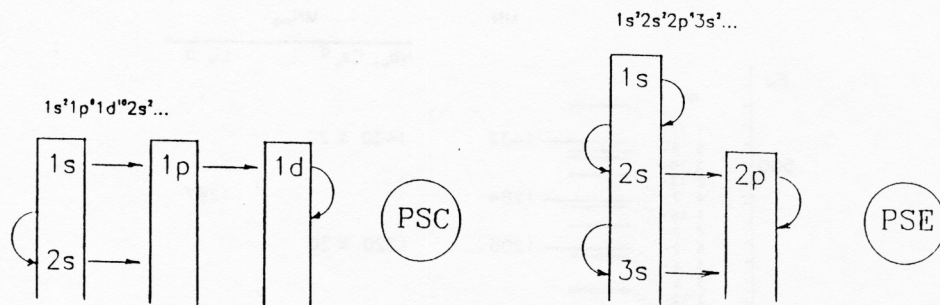
$1s'2s'2p'3s'...$

$1s'1p'1d'^02s'...$

Figure 2. Number and structure of the main groups of both the Periodic System of (alkali metal) Clusters (PSC) and Periodic System of Elements (PSE) are defined by the four deepest states of the aufbau principle only.

Subshell closing that generates magic numbers MN is given in Figure 3 in bold letters together with the corresponding MN as an upper index. Thus, we get a satisfactory result: magic clusters are mainly main group clusters of the following closed shell types

$n\mathrm{s}^2$-type (alkaline earth analoga from PSE):

$$M_2, \; M_{20}, \; M_{92}, \; M_{198}, \; M_{440}, \; M_{832}, \; ...$$

$n\mathrm{p}^6$-type (noble gas analoga from PSE):

$$M_8, \; M_{40}, \; M_{138}, \; M_{338}, \; M_{562}, \; M_{1012}, \; ...$$

$1\mathrm{d}^{10}$-type:

$$M_{18}$$

and less frequent subgroup clusters

$n\mathrm{f}^{14}$-, $n\mathrm{g}^{18}$-,...-type:

$$M_{34}, \; M_{58}, \; M_{268}, \; ...$$

Now, we use the interesting »giant atom concept« of clusters (cf. Ref. 27)

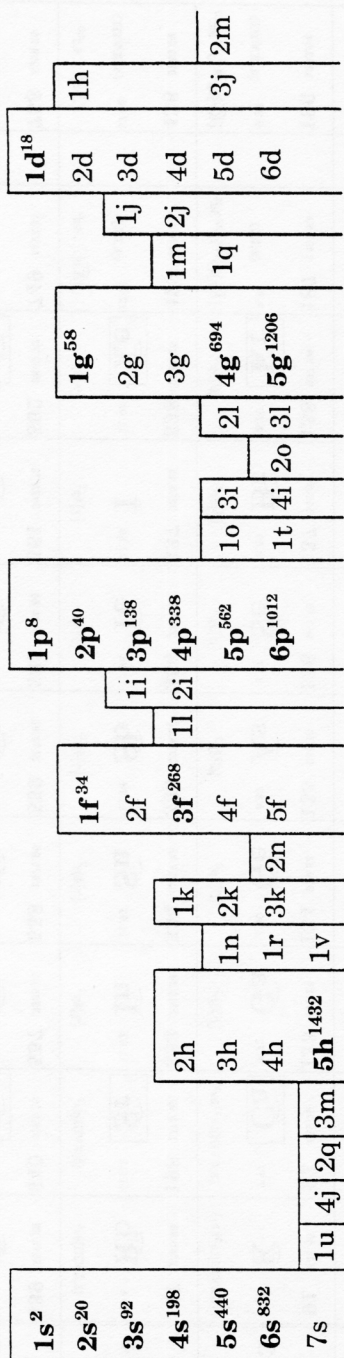$$M_N \equiv \widehat{\mathbf{A}} \tag{2}$$

Figure 3. Fine structure of the open Periodic System of (alkali metal) Clusters (PSC): it exhibits 18 main groups (s-, p-, d-clusters) and an infinite number of subgroups. Subshell closing which generates magic numbers (MN) is given in bold letters together with the corresponding MN as a superscript.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	IXA	...	XVIIIA
1	1 6.939 $\widehat{\text{Li}}$ 1.72 $1s^1$	2 13.878 $\boxed{\text{Be}}$ 2.16 $1s^2$	3 20.817 $\widehat{\text{B}}$ 2.46 $1s^2 1p^1$	4 27.756 $\widehat{\text{C}}$ 2.73 $1s^2 1p^2$	5 34.695 $\widehat{\text{N}}$ 2.94 $1s^2 1p^3$	6 41.634 $\widehat{\text{O}}$ 3.12 $1s^2 1p^4$	7 48.573 $\widehat{\text{F}}$ 3.29 $1s^2 1p^5$	8 55.512 $\boxed{\text{Ne}}$ 3.44 $1s^2 1p^6$	9 62.451 3.58 (1,IX) $[\widehat{\text{Ne}}]1d^1$	...	18 124.90 4.51 (1,XVIII) $[\widehat{\text{Ne}}]1d^{10}$
2	19 131.84 $\widehat{\text{Na}}$ 4.50 $[1,\text{XVIII}]2s^1$	20 138.78 $\boxed{\text{Mg}}$ 4.67 $[1,\text{XVIII}]2s^2$	35 242.86 $\widehat{\text{Al}}$ 5.63 $[\alpha]2p^1$	36 249.80 $\widehat{\text{Si}}$ 5.68 $[\alpha]2p^2$	37 256.74 $\widehat{\text{P}}$ 5.73 $[\alpha]2p^3$	38 263.68 $\widehat{\text{S}}$ 5.78 $[\alpha]2p^4$	39 270.62 $\widehat{\text{Cl}}$ 5.83 $[\alpha]2p^5$	40 277.56 $\boxed{\widehat{\text{Ar}}}$ 5.88 $[\alpha]2p^6$	59 409.40 6.69 (2,IX) $[\widehat{\text{Ar}}]1g^{18}2d^1$	...	68 471.85 7.02 (2,XVIII) $[\widehat{\text{Ar}}]1g^{18}2d^{10}$
3	91 631.45 $\widehat{\text{K}}$ 7.73 $[2,\text{XVIII}]1A^{22}3s^1$	92 638.39 $\boxed{\widehat{\text{Ca}}}$ 7.77 $[2,\text{XVIII}]1A^{22}3s^2$	133 922.89 $\widehat{\text{Ga}}$ 8.72 $[\beta]3p^1$	134 929.83 $\widehat{\text{Ge}}$ 8.80 $[\beta]3p^2$	135 936.76 $\widehat{\text{As}}$ 8.82 $[\beta]3p^3$	136 943.70 $\widehat{\text{Se}}$ 8.84 $[\beta]3p^4$	137 950.64 $\widehat{\text{Br}}$ 8.86 $[\beta]3p^5$	138 957.58 $\boxed{\widehat{\text{Kr}}}$ 8.89 $[\beta]3p^6$	187 1297.59 9.83 (3,IX) $[\widehat{\text{Kr}}]1_2g^{18}1_3^{30}3d^1$		196 1360.04 9.99 (3,XVIII) $[\widehat{\text{Kr}}]1_2g^{18}1_3^{30}3d^{10}$
4	197 1366.98 $\widehat{\text{Rb}}$ 10.6 $[3,\text{XVIII}]_14s^1$	198 1373.92 $\boxed{\widehat{\text{Sr}}}$ 10.02 $[3,\text{XVIII}]_14s^2$	333 2310.68 $\widehat{\text{In}}$ 11.92 $[\gamma]4p^1$	334 2317.63 $\widehat{\text{Sn}}$ 11.93 $[\gamma]4p^2$	335 2324.57 $\widehat{\text{Sb}}$ 11.94 $[\gamma]4p^3$	336 2331.51 $\widehat{\text{Te}}$ 11.95 $[\gamma]4p^4$	337 2338.45 $\widehat{\text{I}}$ 11.96 $[\gamma]4p^5$	338 2345.39 $\boxed{\widehat{\text{Xe}}}$ 11.98 $[\gamma]4p^6$	429 2976.83 12.97 (4,IX) $[\widehat{\text{Xe}}]...4d^1$	...	438 3039.28 13.05 (4,XVIII) $[\widehat{\text{Xe}}]...4d^{10}$
5	439 3046.22 $\widehat{\text{Cs}}$ 13.07 $[4,\text{XVIII}]5s^1$	440 3053.16 $\boxed{\widehat{\text{Ba}}}$ 13.08 $[4,\text{XVIII}]5s^2$	557 3865.02 $\widehat{\text{Tl}}$ 14.15 $[\delta]5p^1$	558 3871.96 $\widehat{\text{Pb}}$ 14.16 $[\delta]5p^2$	559 3878.90 $\widehat{\text{Bi}}$ 14.17 $[\delta]5p^3$	560 3885.84 $\widehat{\text{Po}}$ 14.18 $[\delta]5p^4$	561 3892.78 $\widehat{\text{At}}$ 14.18 $[\delta]5p^5$	562 3899.72 $\boxed{\widehat{\text{Rn}}}$ 14.19 $[\delta]5p^6$	749 5197.31 15.62 (5,IX) $[\widehat{\text{Rn}}]...5d^1$	...	758 5259.76 15.68 (5,XVIII) $[\widehat{\text{Rn}}]...5d^{10}$
...	...	...	...	...	...	...	...	...	...	...	...

Figure 4. The first eight main groups of the Periodic System of (alkali metal) Clusters (PSC), reformulated using the »giant-atom-concept« of clusters (cf. Eq. (2)) and the names of the analogous elements of the Periodic System of Elements (PSE): »Periodic System of Giant Atoms«.

where $\widehat{A}$ is a so-called »giant atom«, which is characterized by quantum numbers n, l, m like a normal atom. Its one-electron states $E_{nl}/\psi_{nlm}\ (r,\vartheta,\varphi)$ exhibit a $2(2l+1)$ fold degeneracy (*cf.* Figure 1).

If we project the first eight main groups from the PSC, we can reformulate this part of PSC by using the bold letters with hat from Eq. (2) and get a nice form of the main group IA...VIIIA of PSC, the »Periodic System of Giant Atoms« (*cf.* Figure 4) because these giant atoms have analogs to the main group elements from PSE, and so we can take their names, in contrast to clusters M_N from the remaining main groups IXA ....XVIIIA, which have been characterized simply by means of the two coordinates of PSC (number of period, number of main group), *e.g.* $M_9 \equiv (1, IX)$, $M_{18} \equiv (1, XVIII)$.

Figure 5 gives the reader a key for taking the condensed information of the Periodic System of Giant Atoms. The most important number is the giant atomic number N.

relative giant atomic mass M_r

giant atomic number N

40   277.56

giant atomic symbol
$\widehat{Ar} \equiv M_{40}$

5.88

$\widehat{Ar}$

giant atomic radius $R/\text{Å}$

$[\alpha]\ 2p^6$

indicates magic giant atom
(N = magic number)

electron structure
$[\alpha] = [1, XVIII]2s^2 1f^{14}$
$[\beta] = [2, XVIII]1h^{22} 3s^2 2f^{14} 1i^{26}$
$[\gamma] = [3, XVIII]4s^2 2h^{22} 1k^{34} 3f^{14} 1l^{38} 2i^{26}$
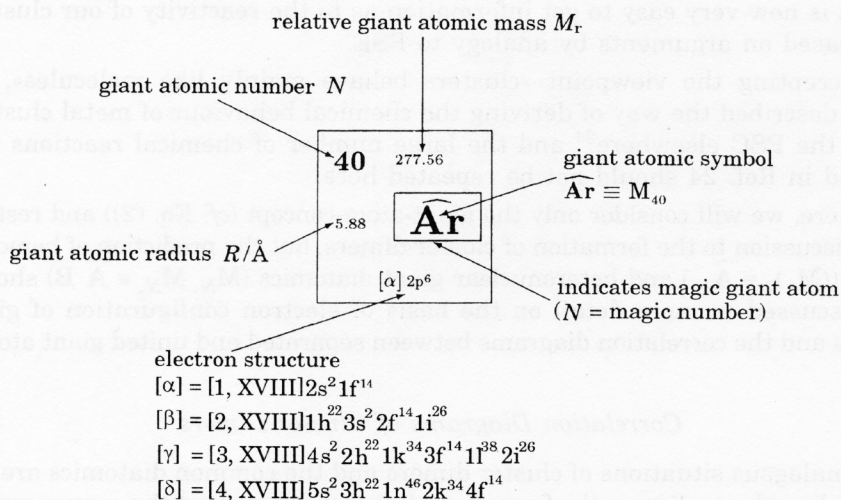$[\delta] = [4, XVIII]5s^2 3h^{22} 1n^{46} 2k^{34} 4f^{14}$

Figure 5. Key to decoding the condensed information within the »Periodic System of Giant Atoms« (*cf.* Figure 4).

This number is related

– to the numerical cluster size of the alkali metal cluster which is behind the giant atomic symbol

$$\widehat{Ar} \equiv M_{40}, \ M = \text{free electron-like metal from PSE}$$

– to the geometrical cluster size (radius R of the jellium sphere)

$$R = r_s N^{1/3} , \quad r_s \sim \text{Wigner-Seitz-Radius} \tag{3}$$

– to the relative atomic mass M_r

$$M_r = N \times A_r(M)$$

All numbers given in PSC are calculated for the special case $M \equiv Li$. Framed giant atomic symbols indicate magic giant atoms $\widehat{A} = M_N$ ($N = MN$). Finally, the electronic structure completes the properties of the giant atoms.

CHEMISTRY OF FREE ELECTRON-LIKE METAL CLUSTERS PREDICTED FROM PSC

It is now very easy to get information as to the reactivity of our clusters M_N based on arguments by analogy to PSE.

Accepting the viewpoint »clusters behave mainly like molecules«, we have described the way of deriving the chemical behaviour of metal clusters from the PSC elsewhere[24] and the large number of chemical reactions discussed in Ref. 24 should not be repeated here.

Here, we will consider only the giant-atom-concept (cf. Eq. (2)) and restrict our discussion to the formation of cluster-dimers, but the prediction of homonuclear (($(M_n)_2 \equiv \widehat{A}_2$) and heteronuclear giant diatomics ($M_{N_1} M_{N_2} \equiv \widehat{A} \, \widehat{B}$) should be discussed in more detail on the basis of electron configuration of giant atoms and the correlation diagrams between separated and united giant atoms.

Correlation Diagrams of Cluster Dimers

Analogous situations of cluster dimers and the common diatomics are obvious. In order to discuss the formation of cluster dimers and the corresponding stability, we have different possibilities of constructing these dimers:

I – A giant dimer may be built by bringing together the whole giant atoms of which it consists. The **separated giant atoms** M_N are characterized by their jellium spheres $R_N = r_s N^{1/3}$ (cf. Eq. 3)).

II – Instead of commencing with infinite separation, we may start with zero cluster separation. That is, we may split the so-called **united giant atom** which is characterized by the jellium sphere for

– equal giant atoms M_N

$$R_{2N} \approx 1.26 \, R_N \tag{4}$$

– unequal giant atoms M_{N_i}, $i = 1, 2$

$$R_{N_1 + N_2} = \left(1 + \frac{N_2}{N_1}\right)^{1/3} R_{N_1}, \quad N_1 > N_2,$$

$$\approx \left(1 + \frac{1}{3}\frac{N_2}{N_1}\right) R_{N_1}, \quad N_1 \gg N_2$$

(5)

III – Finally, we may employ a procedure analogous to that used for giant atoms (*cf.* Figure 1). We add the individual electrons one after another, to the jellium spheres which are regarded as fixed and observe in which jellium orbitals the electrons will arrange themselves (electronic configurations).

For subsequent discussion, it is important to establish in what way the jellium orbitals are altered in the transition from small to large inter-cluster distances and, in particular, into which orbitals of the one limiting case those of the other limiting case go over. Under consideration of certain symmetry constraints (non-crossing rule) using our jellium aufbau principle (Eq. (1)), we obtained cluster correlation diagrams between the jellium orbitals of separated and united giant atoms in the cases of equal (*cf.* Figure 6a) and of unequal giant atoms (*cf.* Figure 6b). These correlation diagrams are very crude schemes, *e.g.* dropping any contribution of hybridization, but even these qualitative schemes are very important for the information about giant molecules (cluster molecules).

Electron Configuration of Cluster Dimers

In order to predict the ground states of cluster dimers from equal giant atoms $\widehat{\mathbf{A}}$, it is necessary to use the jellium orbitals of Figure 6a. With respect to the relatively large equilibrium values of inter-cluster distances of cluster dimers (this situation is characterized by the corresponding jellium spheres drawn at the top of Figure 6a), we use the nomenclature adapted to the separated giant atoms. The vertical broken line gives the approximate position in the diagram (Figure 6a) corresponding to the cluster dimer $\widehat{\mathbf{A}}_2$;
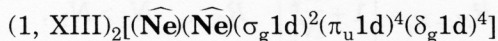
$$e.g. \text{ for } \widehat{\mathbf{Be}}_2 = (M_2)_2$$

in the lowest state, the four valence electrons go into the jellium orbitals $\sigma_g 1s$ and $\sigma_u^* 1s$ which they just fill

$$\widehat{\mathbf{Be}}_2 \ [(\sigma_g 1s)^2 (\sigma_u^* 1s)^2] \text{ and give a bond order}$$

$$\Delta P = P_a - P_b = 1 - 1 = 0$$

which vanishes in contrast, *e.g.* to dimer $(M_{13})_2$

$$(1, \text{XIII})_2[(\widehat{\text{Ne}})(\widehat{\text{Ne}})(\sigma_g 1d)^2(\pi_u 1d)^4(\delta_g 1d)^4]$$

which exhibits a maximum bond order of $\Delta P = 5$. (*cf.* Table III)

In order to predict the ground states of cluster dimers from unequal giant atoms $\widehat{A}$ and $\widehat{B}$, it is necessary to use the jellium orbitals of Figure 6b. If $\widehat{A}$ and $\widehat{B}$ are very different in size, $N_1 >> N_2$, as a consequence, the jellium sphere radii R_{N_1} and R_{N_2} will also be very different and therefore the equilibrium value of the inter-cluster distance will be small. This situation is characterized by the corresponding jellium spheres drawn at the top of Figure 6b (*cf.* Eq. 5)). Thus, it can be assumed that these species approach fairly closelly the united giant atom. In this case, it is more convenient to use the nomenclature adapted to the united giant atom. The vertical broken line gives the approximate position in the diagram (Figure 6b) which corresponds to the cluster dimer $\widehat{A}$ $\widehat{B}$.

Examples:

e.g. for $\widehat{\text{Li}}$ $\widehat{\text{F}} \equiv \text{Li}(\text{Li}_7)$, $N_1 = 1$, $N_2 = 7$, $R_8 \approx 1.05\, R_7$
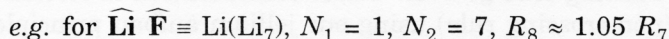
in the lowest state, the eight valence electrons go into the jellium orbitals $1s\sigma$, $1p\sigma$ and $1p\pi$ which they just fill

$$\widehat{\text{Li}}\ \widehat{\text{F}}\ [(1s\sigma)^2(1p\sigma)^2(1p\pi)^4]$$
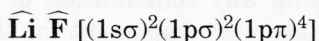
We have estimated, by a preliminary semiempirical method, a stable giant molecule $\text{Li}(\text{Li}_7)$: BE = -1.70 eV, using an optimized pentagonal pyramidal geometry for the giant atom $\widehat{\text{F}}$.

In case of the two similar giant atoms $\widehat{A}$ and $\widehat{B}$ ($N_1 \approx N_2$), we can use the correlation diagram for equal giant atoms

$$\text{e.g.}\ \widehat{\text{C}}\ \widehat{\text{O}} = (M_4)(M_6)[(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2(\pi_u 1p)^4]\quad \Delta = 3$$
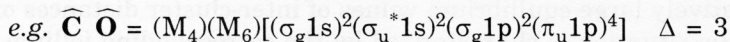
In this case, we have a strong similarity to $\widehat{N}_2$ and get the same electron configuration. Therefore, after these remarks about the unequal giant atoms $\widehat{A}$, $\widehat{B}$, we can restrict ourselves to the case $\widehat{A} + \widehat{A} \rightarrow \widehat{A}_2$.

Tables I – III summarize a number of predictions for the formation of cluster dimers from alkali metal clusters, strictly speaking, from free electron-like metal clusters derived from PSC (Figure 4) and from the correlation diagram (Figure 6a).

It is very interesting to discuss these predictions and to compare them, as far as possible, with experimental data and then compare them with the results calculated by various authors. It is very satisfactory that we get strong support in all cases.
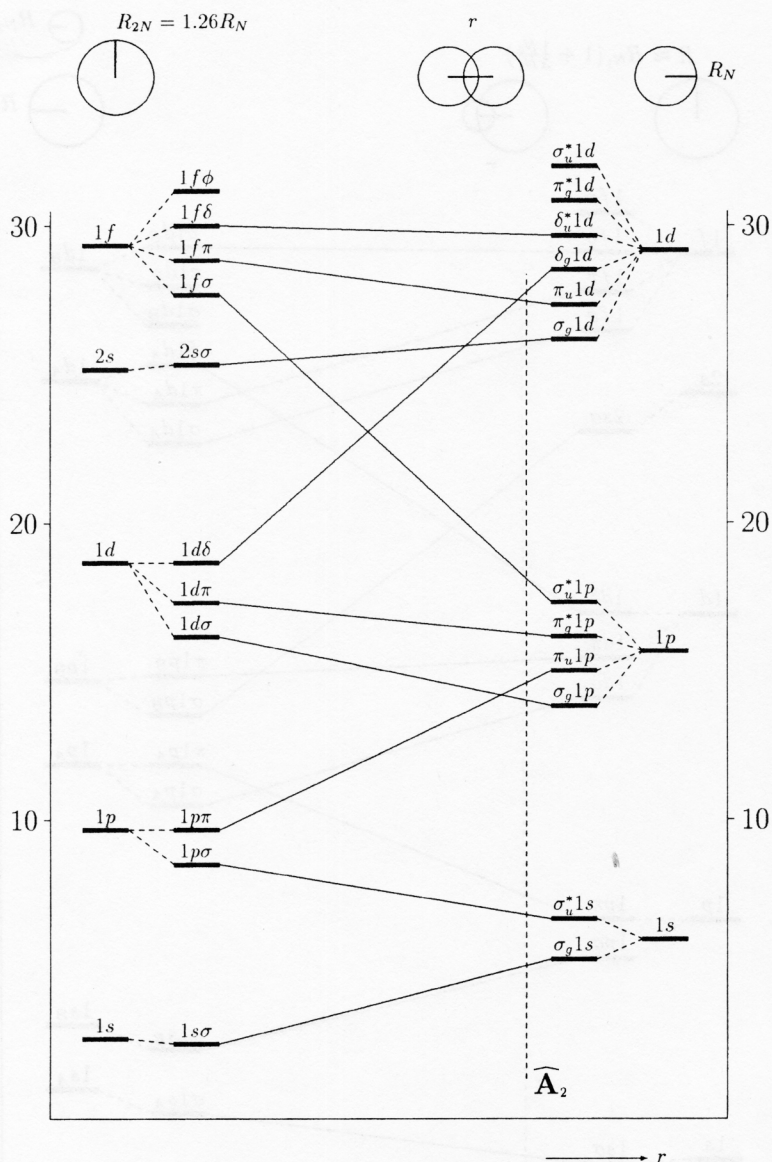
Figure 6a. Correlation of jellium orbitals in a two-jellium-sphere system for equal giant atoms. To the extreme left and the extreme right the jellium orbitals are given in the united and separated giant atoms (clusters), respectively and, besides them, those in the giant molecules (cluster-dimers) for very small and very large inter-cluster distances, respectively. The region in between corresponds to intermediate inter-cluster distances. The vertical broken line gives the approximate position in the diagram corresponding to a cluster dimer $\widehat{\mathbf{A}}_2$.
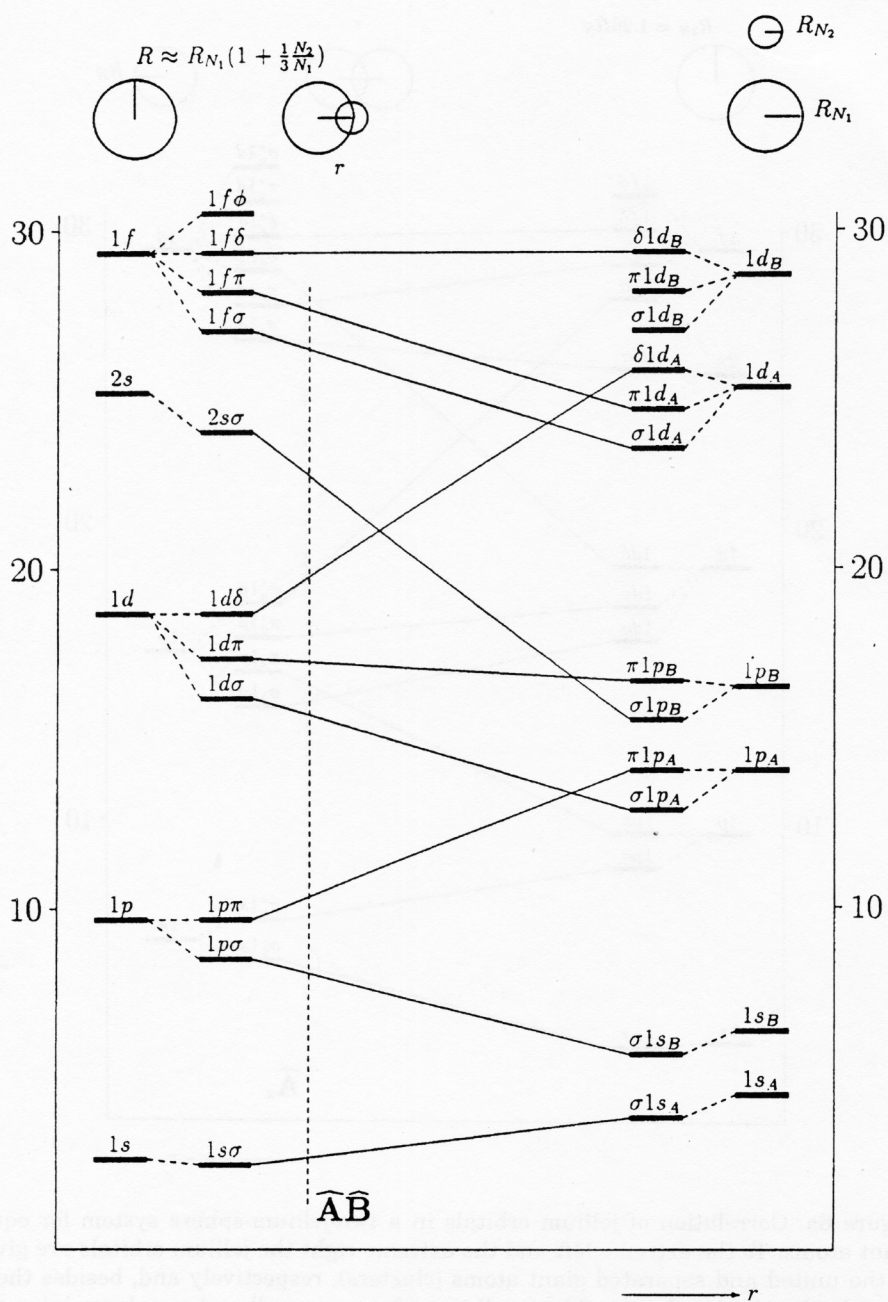
Figure 6b. Correlation of jellium orbitals in a two-jellium-sphere system for unequal giant atoms. See the remarks for Figure 6a.

DISCUSSION

Prediction of the Stability of Cluster Dimers

Dimers of giant atoms from the first period of PSC (IA...VIIIA)

The last column of Table I contains examples of cluster dimers that support our predictions.

IA-group ($\Delta = 1$)

Here, the assertion is trivial $(M_1)_2 \equiv M_2$:

	Li_2	Na_2	K_2	...
$-BE/eV$	1.08	0.75	0.51	...

IIA-group ($\Delta = 0$)

$\Delta = 0$ corresponds to the non-existence of a covalent bound dimer. This means that, if at all, only, a van der Waals-dimer exists, based on very weak dispersion forces. This is exactly the result of our quantum chemical calculation of $(Li_2)_2$ by means of the density functional theory (DFT) with non-local exchange/correlation terms:[28]

$Li_2 ... Li_2$	r_e/pm	$-BE/eV$
parallel	582	0.01
linear	604	0.14

On the basis of MRD-CI procedure (multireference diexcitation-configuration interaction), Boustani *et al.*[29] calculated a linear dimer Li_2-Li_2 with $-BE < 0.01$ eV.

IIIA-group ($\Delta = 1$)

Since our model is not only valid for alkali metal clusters but also for earth metal clusters, we can transform

$(M_3)_2 \equiv (M(IA)_3)_2 \hat{=} (M(IIIA)_1)_2 \equiv M(IIIA)_2$:

	B_2	Al_2	Ga_2
$-BE/eV$	2.83	1.99	1.39

and have a simple confirmation for the predicted $\Delta = 1$.

IVA-group ($\Delta = 2$)

Investigation of the bond properties of sodium cluster dimers $(Na_4)_2$ by linear combination of jellium orbitals (LCJO) by Ishii et al.[30] shows that two Na_4 clusters attract each other strongly and, therefore, give strong support to our prediction of stable dimers $(Na_4)_2$: BE = −0.495 eV, r_e = 628 pm.

VIIA-group ($\Delta = 1$)

We have shown the existence of a stable giant dimer $\widehat{F}_2$: BE = −1.04 eV by preliminary semiempirical calculations of $(Li_7)_2$. The giant $\widehat{F}$-atom Li_7 exhibits a pentagonal-bipyramidal geometry.

VIIIA-group ($\Delta = 0$)

In accordance with the closed shell electronic structure of the giant $\widehat{Ne}$ atom, our semiempirical calculation of $(Li_8)_2$ gives BE > 0 !

But, there is also strong evidence by much better calculations on $(Na_8)_2$. Ishii et al.[30] have found (LCJO-DFT in LDA) that Na_8 has an inert property because the force between jellium spheres in $(Na_8)_2$ is due to a weak dispersion force only: $(Na_8)_2$: BE = −0.073 eV, r_e = 846 pm.

Very interesting simulations of cluster-cluster collisions (CCC) combined with DFT in LDA within the double magic system $Na_8 + Na_8$ give information on an unstable »Na_8Na_8-molecule« in contrast to the stable cluster-molecule Na_9Na_9 (IXA group) (Schmidt et al.,[31] Seifert et al.[32]).

Dimers of giant atoms from the second period of PSC (IA...VIIIA)

Although the giant atoms within the second period are much larger than in the first period, we have five examples that confirm the predicted formation of dimers.

IA-group ($\Delta = 1$)

Saito et al.[33] report that a dimer of clusters, $(Na_{19})_2$, is energetically stable and explain the abundance of Na_{38} in sodium-cluster mass spectra. A fusion process of two Na_{19} clusters has been studied by these authors on the basis of the jellium-sphere background model by the DFT/LDA method. The calculated binding energy of −0.9 eV shows that the force between two clusters is attractive and that the complete fusion is preceded by the formation of a stable $(Na_{19})_2$ dimer. This dimer is separated by a barrier of 1.4 eV from the giant united atom Na_{38}.

Knospe et al.[34] have calculated the inter-cluster potential for the systems Na_NNa_N (N = 8, 9, 19, 20) on the basis of DFT/LDA and the jellium model.

TABLE I

Valence electron configurations and bond orders of the ground states of giant molecules composed of equal giant atoms from the **first** period and the **first eight** main groups IA...VIIIA of the Periodic System of (alkali metal) Clusters (PSC).

mgr	cluster-dimer	valence electron configuration	P_b	P_a	ΔP	examples ($-BE$/eV)
		1st period of PSC; main groups (mgr) IA ... VIIIA				
IA	$(M_1)_2 = \widehat{\mathbf{Li}_2}$	$(\sigma_g 1s)^2$	1	–	1	Li_2 (1,08), Na_2 (0.75), K_2 (0.51),...
IIA	$(M_2)_2 = \widehat{\mathbf{Be}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2$	1	1	0	$(Li_2)_2$*,[28,29]
IIIA	$(M_3)_2 = \widehat{\mathbf{B}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2$	2	1	1	B_2 (2.83), Al_2 (1.99), Ga_2 (1.39),...
IVA	$(M_4)_2 = \widehat{\mathbf{C}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2(\pi_u 1p)^2$	3	1	2	$(Na_4)_2$ (0.49)[30]
VA	$(M_5)_2 = \widehat{\mathbf{N}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2(\pi_u 1p)^4$	4	1	3	
VIA	$(M_6)_2 = \widehat{\mathbf{O}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2(\pi_u 1p)^4(\pi_g^* 1p)^2$	4	2	2	
VIIA	$(M_7)_2 = \widehat{\mathbf{F}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2(\pi_u 1p)^4(\pi_g^* 1p)^4$	4	3	1	$(Li_7)_2$ (1.04)*
VIIIA	$(M_8)_2 = \widehat{\mathbf{Ne}_2}$	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 1p)^2(\pi_u 1p)^4(\pi_g^* 1p)^4(\sigma_u^* 1p)^2$	4	4	0	$(Li_8)_2$ (< 0)*, $(Na_8)_2$[30-32]

* this work

TABLE II

Valence electron configurations and bond orders of the ground states of giant molecules composed of equal giant atoms from the **second** period and the **first eight** main groups IA...VIIA of the Periodic System of (alkali metal) Clusters (PSC).

mgr	cluster-dimer	2nd period of PSC; main groups (mgr) IA ... VIIA valence electron configuration	P_b	P_a	ΔP	examples (−BE/eV)
IA	$(M_{19})_2 = \widehat{Na_2}$	$aa(\sigma_g 2s)^2$	1	–	1	$(Na_{19})_2$ $(1.4)^{33}$
IIA	$(M_{20})_2 = \widehat{Mg_2}$	$aa(\sigma_g 2s)^2(\sigma_u^* 2s)^2$	1	1	0	$(Na_{20})_2{}^{34}$
IIIA	$(M_{35})_2 = \widehat{Al_2}$	$bb(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2$	2	1	1	
IVA	$(M_{36})_2 = \widehat{Si_2}$	$bb(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^2$	3	1	2	$(Al_{12})_2$ $(4.2)^*$
VA	$(M_{37})_2 = \widehat{P_2}$	$bb(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4$	4	1	3	
VIA	$(M_{38})_2 = \widehat{S_2}$	$bb(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$	4	2	2	
VIIA	$(M_{39})_2 = \widehat{Cl_2}$	$bb(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4$	4	3	1	$(Al_{13})_2$ $(4.68)^{*,35,36}$
VIIIA	$(M_{40})_2 = \widehat{Ar_2}$	$bb(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4(\sigma_u^* 2p)^2$	4	4	0	$(Al_{12}Si)_2$ $(0.06)^{35,36}$

a ≡ $1s^2 1p^6 1d^{10}$ = [(1, XVIII)]

b ≡ $a 1f^{14}$

* this work

These potentials show, among other things, stable dimers $(Na_{19})_2$ (and $(Na_9)_2$ (IXA-group) characterized by deep minima and the corresponding potential barriers.

IIA-group ($\Delta = 0$)

The same authors (Knospe et al.[34]) observed the opposite effect for the double magic systems $Na_{20} + Na_{20}$ (and $Na_8 + Na_8$, VIIIA-group), in full analogy to the diatomics Mg_2 (and Ne_2).

IVA- and VIIA-group ($\Delta = 2$ and $\Delta = 1$)

We have shown again, by preliminary semiempirical calculations, the existence of stable giant dimers $\widehat{Si}_2$, (BE = −4.2 eV) and $\widehat{Cl}_2$ (BE = −4.7 eV) using optimized icosahedral geometry for the clusters Al_{12} and Al_{13}, respectively.

Further support is given by Ikeda et al.[35,36], who calculated stable $(Al_{13})_2$ (BE = −0.17 eV, r_e = 677 pm) (VIIIA-group).

VIIIA-group ($\Delta = 0$)

Closed shell systems like $\widehat{Ar}$ are always most interesting, in our case the double magic dimer $M_{40}M_{40}$. First principle calculations for $(Al_{12}Si)$ (and Al_{13}, Au_{13}, $Au_{12}Cr$) using icosahedral symmetry were performed by the self-consistent local density functional scheme including the norm-conserving pseudopotential in the LCAO method by Ohnishi et al.[35,36] By doping Si into Al_{12} (in order to get a 40 electron cluster), these authors found stabilization by 0.2 eV/atom. Interactions between $(Al_{12}Si)$... $(Al_{12}Si)$ are discussed based on the Harris functional scheme and the authors found as expected $(Al_{12}Si)_2$ (BE = −0.06 eV, r_e = 740 pm), a weakly bound dimer only.

Dimers of giant atoms from the first period of PSC (IXA...XVIIIA)

In this chapter, we leave that part of PSC: IA...VIIIA which has analogous relations to PSE, which means that we are looking for the conditions within the last ten main groups IXA...XVIIIA without any direct relation to PSE.

We use again the simple form of our correlation diagrams.

We can extract from Figure 6a (upper part on the right hand side) the aufbau principle for giant dimers, as summarized in Table III. Due to the existence of five jellium d-orbitals, we are able to construct bond orders up to five and we found the maximum in the main group XIIIA

$$(1, XIII)_2[(\sigma_g 1d)^2 \, (\pi_u 1d)^4 (\delta_g 1d)^4], \Delta = 5$$

TABLE III

Valence electron configurations and bond orders of the ground states of giant molecules composed of equal giant atoms from the first period and the last ten main groups IXA...XVIIIA of the Periodic System of (alkali metal) Clusters (PSC).

| mgr	cluster-dimer	valence electron configuration			P_b	P_a	ΔP	examples (–BE/eV)
		1st period of PSC; main groups (mgr) IXA ... XVIIIA						
IXA	$(M_9)_2 = (1, IX)_2$	$(\sigma_g 1d)^2$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	1	–	1	$(Na_9)_2$ [31,32,34]
XA	$(M_{10})_2 = (1, X)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^2$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	2	–	2	
XIA	$(M_{11})_2 = (1, XI)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^4$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	3	–	3	
XIIA	$(M_{12})_2 = (1, XII)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^4(\delta_g 1d)^2$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	4	–	4	$(Li_{12})_2$ (1.40)*
XIIIA	$(M_{13})_2 = (1, XIII)_2$	$(\sigma_g 1s)^2(\pi_u 1d)^4(\delta_g 1d)^4$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	5	–	5	$(Li_{13})_2$ (1.20)*, $(Au_{13})_2$ (0.26)[35,36]
XIVA	$(M_{14})_2 = (1, XIV)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^4(\delta_g 1d)^4(\delta_u^* 1d)^2$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	5	1	4	
XVA	$(M_{15})_2 = (1, XV)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^4(\delta_g 1d)^4(\delta_u^* 1d)^4$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	5	2	3	
XVIA	$(M_{16})_2 = (1, XVI)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^4(\delta_g 1d)^4(\delta_u^* 1d)^4(\pi_g^* 1d)^2$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	5	3	2	
XVIIA	$(M_{17})_2 = (1, XVII)_2$	$(\sigma_g 1s)^2(\pi_u 1s)^4(\delta_g 1d)^4(\delta_u^* 1d)^4(\pi_g^* 1d)^4$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	5	4	1	
XVIIIA	$(M_{18})_2 = (1, XVIII)_2$	$(\sigma_g 1d)^2(\pi_u 1d)^4(\delta_g 1d)^4(\delta_u^* 1d)^4(\pi_g^* 1d)^4(\sigma_g^* 1d)^2$	$\overset{\frown}{Ne}$	$Ne\overset{\frown}{Ne}$	5	5	0	$(Au_{12}Cr)_2$ (0.16)[35,36]

$\overset{\frown}{Ne} \equiv 1s^2 1p^6$

* this work
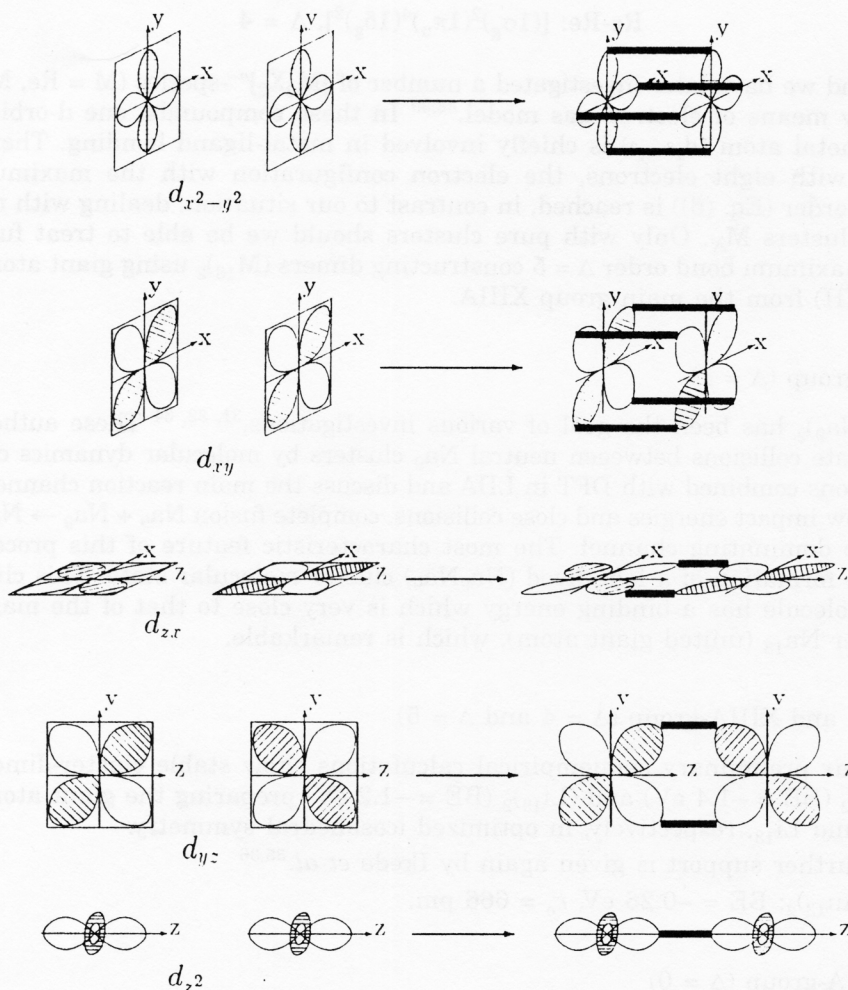
Figure 7. The overlapping possibilities of the five d-orbitals between two giant atoms from the main groups IXA...XVIIIA of the Periodic System of (alkali metal) Clusters (PSC). From bottom to top: one σ-, two π- and two δ-bonds.

This orbital scheme is illustrated in Figure 7, showing the overlapping possibilities of the five d-orbitals and the resulting three types of MO's: σ-, π- and δ-orbitals.

This part of PSC is especially interesting to chemists, because inorganic chemists are familiar with multiple metal-metal bonds with $\Delta > 3$ in cluster compounds, strictly speaking in dinuclear cluster compounds. In 1965, Cotton[37] discovered in the species $[Re_2Cl_8]^{2-}$ the first 4-fold bond

$$\text{Re-Re: } [(1\sigma_g)^2(1\pi_u)^4(1\delta_g)^2], \; \Delta = 4 \tag{6}$$
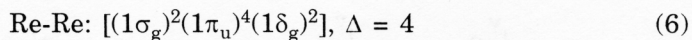
and we have later investigated a number of $[M_2X_2]^{n-}$-species (M = Re, Mo, Tc) by means of electron gas model.[38,39] In these compounds, one d-orbital per metal atom ($d_{x^2-y^2}$) is chiefly involved in metal-ligand bonding. Therefore, with eight electrons, the electron configuration with the maximum bond order (Eq. (6)) is reached, in contrast to our situation, dealing with naked clusters M_N. Only with pure clusters should we be able to treat fully the maximum bond order $\Delta = 5$ constructing dimers $(M_{13})_2$ using giant atoms (1, XIII) from the main group XIIIA.

IXA-group ($\Delta = 1$)

$(Na_9)_2$ has been the goal of various investigations,[31, 32, 34] These authors simulate collisions betweeen neutral Na_9 clusters by molecular dynamics calculations combined with DFT in LDA and discuss the main reaction channels. For low impact energies and close collisions, complete fusion $Na_9 + Na_9 \rightarrow Na_{18}$ is the dominating channel. The most characteristic feature of this process is the formation of a long-lived (Na_9Na_9) cluster molecular state. This cluster-molecule has a binding energy which is very close to that of the magic cluster Na_{18} (united giant atom), which is remarkable.

XIIA- and XIIIA-group ($\Delta = 4$ and $\Delta = 5$)

Our preliminary semiempirical calculations show stable cluster-dimers $(Li_{12})_2$ (BE = −1.4 eV) and $(Li_{13})_2$ (BE = −1.2 eV) preparing the giant atoms Li_{12} and Li_{13}, respectively, in optimized icosahedral symmetry.

Further support is given again by Ikeda et al.[35,36]

$(Au_{13})_2$: BE = −0.26 eV, r_e = 666 pm.

XVIIIA-group ($\Delta = 0$)

As an example for a weakly bound closed shell dimer, we will mention the calculation by Ikeda et al.[35,36] once more. By doping Cr into Au_{12} in order to get a 18 electron cluster, these authors found a stabilization by 0.7 eV/atom. By calculating the interaction between $(Au_{12}Cr)...(Au_{12}Cr)$, they got an expected weakly bound dimer $(Au_{12}Cr)_2$ (BE = −0.16 eV, r_e = 674 pm).

SOME REMARKS TO OTHER FORMS OF CLUSTER-MATTER

The reactivity of free electron-like metal clusters is a very broad field of chemistry. In this paper, we have discussed a very simple part of this interesting and current field, the formation of cluster-dimers $\widehat{A}_2$, including a short reference to giant molecules $\widehat{A} \; \widehat{B}$.

We have pointed to some other examples of cluster-matter in Ref. 24. Preliminary calculations show the possibility of constructing stable giant ionic lattices, *e.g.* $\widehat{\text{Li}}\,\widehat{\text{F}} \equiv M_1{}^+(M_7{}^-)$ or $\widehat{\text{Na}^+}\,\widehat{\text{Cl}^-} \equiv (M_{19}^+)(M_{39}^-)$. Systems like $Li^+(Li_7^-)$, $(Li_{19}^+)(Li_{39}^-)$, $(Li_{19}^+)(Al_{13}^+)$,... belong to the group of new metals and alloys, respectively.

An iterative application of our model (the suppositions of such a procedure are fulfilled)

$$\text{model}\{M\} = \widehat{\mathbf{M}} \equiv M_N$$

$$\text{model}\{\widehat{\mathbf{M}}\} = \widehat{\mathbf{M}}^{(2)} \equiv \widehat{\mathbf{M}}_N$$

$$\text{model}\{\widehat{\mathbf{M}}^{(2)}\} = \widehat{\mathbf{M}}^{(3)} \equiv \widehat{\mathbf{M}}^{(2)}{}_N$$

generates a principle for constructing new metals (cluster-metals)

$$\ldots \equiv \widehat{\mathbf{M}}^{(3)} \equiv \widehat{\mathbf{M}}^{(2)}{}_N \equiv (\widehat{\mathbf{M}}_N)_N \ldots ((M_N)_N)_N \ldots$$

G. Schmid[40–42] has generated experimentally cluster-metals of this type, starting with M_{13} building blocks and ending with $\ldots ((M_N)_N)_N \ldots$ -particles, μm in size. He realized this construction principle for metals like Au and others and gave strong experimental support to our model.

CONCLUSION

Nowadays, we can apply simple potential models formerly used by nuclear physicists to describe magic numbers of atomic nuclei, in a more sophisticated version, to calculate with the same success electronic shell structures of free electron-like metal clusters.

By means of such a model, optimized for alkali metal clusters, the experimentally observed magic numbers can be explained up to 1432 electrons.

In this paper, we use the conceptually and computationally simple jellium model to test additional features of the giant atom concept of clusters and we generate a Periodic System of (alkali metal) Clusters (PSC) on the basis of the calculated aufbau principle.

We have now a very interesting tool for deriving the whole chemistry of free electron-like metal clusters. Exemplarily, we discuss the formation of cluster dimers. But, because the power of this tool is much stronger, we are able to derive various new forms of cluster-matter (cluster-molecules, cluster-crystals, cluster-metals, *etc.*) which may be applicable to new material designs, too.

It should be mentioned that the electronic shell structure is not only one of the most prominent phenomena in cluster science but the shell structure will also provide new insights for understanding the chemical properties of clusters. However, it should also be mentioned that much work has also to be done to confirm many unconventional predictions.

We hope our model calculations will give many thought – provoking impulses both for new experiments (computer experiments included) and for new calculations.

REFERENCES

1. G. Gamow, *Nature* **131** (1933) 433.
2. H. Margenau, *Phys. Rev.* **46** (1934) 613.
3. W. Heisenberg, *Z. Phys.* **96** (1935) 473.
4. H. A. Bethe and R. Bacher, *Rev. Mod. Phys.* **8** (1937) 82.
5. W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, *Phys. Rev. Lett.* **52** (1984) 2141.
6. W. Begemann, S. Dreihofer, K. H. Meiwes-Broer, and H. O. Lutz, *Z. Phys. D: At. Mol. Clusters* **3** (1986) 183.
7. T. Bergmann, H. Limberger, and T. P. Martin, *Phys. Rev. Lett.* **60** (1988)1767.
8. J. L. Martins, R. Car, and J. Buttet, *Surf. Sci.* **106** (1981) 265.
9. W. Ekardt, *Ber. Bunsen-Ges. Phys. Chem.* **88** (1984) 289.
10. K. Clemenger, *Phys. Rev.* **B 32** (1985) 1359.
11. Y. Ishii, S. Ohnishi, and S. Sugano, *Phys. Rev.* **B 33** (1986) 5271.
12. T. Bergmann and T. P. Martin, *J. Chem. Phys.* **90** (1989) 2848.
13. S. Bjørnholm, J. Borggreen, O. Echt, K. Hansen, J. Pederson, and H. D. Rasmussen, *Phys. Rev. Lett.* **65** (1990) 1627.
14. T. P. Martin, T. Bergmann, H. Göhlich, and T. Lange, *J. Phys. Chem.* **95** (1991) 6421.
15. T. P. Martin, T. Bergmann. H. Göhlich, and T. Lange, in: G. Pacchioni *et al.* (Eds.) *Cluster Models for Surface and Bulk Phenomena*, New York, Plenum Press, 1992.
16. H. Göhlich, T. Lange, T. Bergmann, and T. P. Martin, *Phys. Rev. Lett.* **65** (1990) 748.
17. T. P. Martin, T. Bergmann, H. Göhlich, and T. Lange, *Chem. Phys. Lett.* **172** (1990) 209.
18. C. Brechignac, Ph. Cahuzac, M. de Frutos, J.-Ph. Roux, and K. Bowen, in : P. Jena *et al.* (Eds.) *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, Kluwer Academic Publishers, 1992.
19. J. L. Persson, R. L. Whetten H.-P. Cheng, and R. S. Berry, *Chem. Phys. Lett.* **186** (1991) 215.
20. M. Broyer, Abstracts of 2nd International Conference on Atomic and Nuclear Clusters '93, Santorini, Greece, 28. 6. – 3.7. 1993.
21. M. Broyer, *Phys. Rev.* (in press).
22. H. Müller, Ch. Opitz, and M. Müller, Abstracts of 2nd International Conference on Atomic and Nuclear Clusters '93, Santorini, Greece, 28. 6. – 3. 7. 1993.
23. H. Müller and Ch. Opitz, Abstracts of 29. Symposium für Theoretische Chemie, Oberwiesenthal, Germany, 27. 9. – 1. 10. 1993.

24. H. Müller and Ch. Opitz, *Z. Phys. Chem.* **187** (1994) 179.
25. H. Müller and Ch. Opitz, Abstracts of 8th International Congress of Quantum Chemistry (ICQC), Prague, 19.–23. 6. 1994.
26. H. Müller and Ch. Opitz, Abstracts of 30. Symposium für Theoretische Chemie, Fiesch, Switzerland, 11.–15. 9. 1994.
27. M. L. Cohen, in: S. Sugano, Y. Nishima and S. Ohnishi (Eds,.) *Microclusters*, Springer, Berlin, 1987, p. 2.
28. P. Mlynarski and H. Müller, unpublished results.
29. I. Boustani, W. Pewestorf, P. Fantucci, V. Bonačić-Koutecky, and J. Koutecky, *Phys. Rev.* **B 35** (1987) 9437.
30. Y. Ishii, S. Saito, and S. Ohnishi, *Z. Phys. D: At Mol. Clusters* **7** (1987) 289.
31. R. Schmidt, G. Seifert, and H. O. Lutz, *Phys. Rev. Lett* **A 158** (1991) 231.
32. G. Seifert, R. Schmidt, and H. O. Lutz, *Phys. Rev. Lett.* **A 158** (1991) 237.
33. S. Saito and S. Ohnishi, *Phys. Rev. Lett.* **59** (1987) 190.
34. O. Knospe, R. Schmidt, E. Engel, U. R. Schmidt, R. M. Dreizler, and H. O. Lutz, *Phys. Lett.* **A 183** (1993) 332.
35. T. Ikeda and S. Ohnishi, in: P. Jena (Ed.) *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, Vol. I, Kluwer Academic Publishers, 1992, p. 559.
36. S. Ohnishi, T. Ikeda, and N. Watari, *Nanotechnology* **3** (1992) 173.
37. F. A. Cotton, *Inorg., Chem.* **4** (1965) 334.
38. H. Müller, *Z. Phys. Chem.* (Leipzig) **248** (1971) 152.
39. Ch. Opitz, H. Müller, and R. Kästner, *Wiss. Z. Friedrich-Schiller-Univ. Jena, Math.-Naturwiss. Reihe* **31** (1982) 943.
40. G. Schmid, *Nachr. Chem. Tech. Lab.* **34** (1987) 249.
41. G. Schmid, *Chemie in unserer Zeit* **22** (1988) 85.
42. G. Schmid, *Polyhedron* **7** (1988) 2321.

SAŽETAK

Periodni sustav metalnih klustera – izvor različitih oblika »klusterske materije«

Hans Müller i Christian Opitz

Jednostavni modificirani model »jellium« dopušta izračunavanje svih magičnih brojeva velikih metalnih klustera M_N do $N = 1432$ i dobro se slaže s eksperimentalnim podacima. Ti rezultati dopuštaju slijedeće zaključke temeljene na rečenom modelu: (I) računi zasnovani na načelu izgradnje omogućuju sastavljanje periodnog sustava klustera (alkalijski metali) PSC; (II) PSC, točnije periodni sustav »velikih atoma« moćno je sredstvo za predviđanje reaktivnosti metalnih klustera sa slobodnim elektronima; (III) posebno se raspravlja o stvaranju dimernih klustera, a rezultati su u skladu s eksperimentalnim i teorijskim iskustvom; (IV) razni oblici »klusterske materije« istaknuti su u odnosu na nove materijale; (V) potrebno je još mnogo truda da se potvrde neka nekonvencionalna predviđanja; nužni su novi eksperimenti i proračuni.