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A jellium study of two-component metal clusters

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Abstract. The spherical jellium model is applied in studying the electronic properties of colloids/clusters consisting of two types of metal. Although the jellium model is far from exact, it can give insight into the overall properties of these systems that otherwise are too complex for most other electronic structure studies. Special emphasis is put on the stability as a function of system size for which it is found that both metals contribute to the regularity with which particularly stable systems occur, and on the Fermi energy as a function of system size. The latter is of relevance in the catalytic activity of such systems, that has been studied experimentally, and is found to display an oscillatory behaviour that correlates with that of the relative total energy but also to be overall lower than that of the pure systems consisting of only one type of atoms.

1. Introduction

The number of studies of the properties of nanostructured materials has grown enormously during the last 1–2 decades partly due to the improved techniques for controlled synthesis of increasingly monodisperse systems and partly due to the improved theoretical models and methods for describing their properties. One class of such materials consists of clusters of simple metals. When they contain only one type of atoms they show the existence of so-called magic numbers, i.e., sizes for which the clusters are particularly stable. It was early realized that this, to a large extent, was dictated by the essentially spherical symmetry of the system and that a simple jellium model, i.e., a model according to which the valence electrons move in an external potential due to the core electrons and the nuclei that is approximated as being the electrostatic potential of a spherically symmetric, homogeneous jellium, can account qualitatively for many of the experimental observations for these systems (references [1–5]; see also [6–8]). According to this model, the electrons move in a spherical potential, and the orbitals can be written as a radial part times a harmonic function. Then, the magic numbers correspond to systems for which all (l, m) shells are completely filled or empty. As the system size grows the particular stability of such magic-number systems becomes less pronounced but can still be recognized for systems with up to above 10 000 valence electrons (see, e.g., [9]).

During the last decade it has also become possible to synthesize metal clusters containing two, or even three, different metals that then form largely concentric parts of an essentially spherical nanoparticle [10–20] Although these clusters, or colloids, often are somewhat larger (i.e., they contain several 1000 atoms) than the single-metal clusters for which the occurrence of magic numbers is of dominating importance, the possibility of synthesizing largely monodispersive systems has led to the observation of size-dependent properties (for instance catalytic) [19]. These results raise the question of whether clusters or colloids

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containing two types of metal atoms possess properties similar to those of the clusters with only one type of metal atoms.

It is the purpose of the present communication to address this question. To this end we shall apply the simplest possible jellium model. This model suffers from a number of approximations that partly will be discussed below, but is on the other hand so simple that it allows for a more systematic study of a larger number of systems that with more elaborate methods would become prohibitively complicated due to the size and low symmetry of the systems of interest. The questions that we shall concentrate on are (i) whether such systems also show magic numbers and how the different properties of the two metal atoms dictate this property, and (ii) whether the energies of the orbitals closest to the Fermi level show a behaviour that can explain the size dependence of the catalytic properties.

For the sake of completeness we mention that Ekardt [21] reported results of a similar study which, however, was restricted to much smaller systems. Different, more accurate, methods were applied by Alonso and co-workers [22,23], Christensen *et al* [24], and Rey *et al* [25] but once again for significantly smaller systems than those of the present work. These methods do, however, possess the important difference from the present work that the positions of the nuclei were explicitly included in the calculations.

The paper is organized as follows. In section 2 we present briefly our computational method and discuss some of the problems related to the jellium approximation. Section 3 is devoted to results for clusters of Ni and Cu atoms, and section 4 to those for clusters of Au and Cd atoms. It shall be strongly emphasized that due to the jellium approximation the results cannot be considered anything but giving a qualitative description of those systems but, on the other hand, that the general findings may also apply to other bimetallic clusters. Finally, section 5 contains the main conclusions.

2. Computational method

All systems of interest to us are assumed to be spherically symmetric. Moreover, the potential of the core electrons and the nuclei for each metal separately is treated within a jellium approximation. The Hohenberg–Kohn density-functional formalism [26] leads then to the following single-particle Kohn–Sham [27] equations:

$$\hat{h}_{\text{eff}}\psi_i(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \tag{1}$$

with the potential

$$V(\vec{r}) = V_{\text{C}}(\vec{r}) + V_{\text{xc}}(\vec{r}) + V_{\text{jel}}(\vec{r}) \tag{2}$$

which is the sum of the Coulomb potential of the valence electrons, their exchange–correlation potential, and the Coulomb potential of the jellium. Due to the spherical symmetry, each term of equation (2) is spherically symmetric, the eigenfunctions ψ_i of equation (1) separate into a radial dependence times a harmonic function, and the Kohn–Sham equations are in effect one dimensional and can be solved numerically. Then, the total energy is given as

$$\begin{aligned} E_{\text{tot}} &= \sum_{i=1}^{\text{occ}}\langle\psi_i|-\frac{\hbar^2}{2m}\nabla^2|\psi_i\rangle + \int\left[\frac{1}{2}V_{\text{C}}(\vec{r}) + V_{\text{jel}}(\vec{r}) + \epsilon_{\text{xc}}(\vec{r})\rho(\vec{r})\right]\mathrm{d}\vec{r} \\ &= \sum_{i=1}^{\text{occ}}\epsilon_i + \int\left[-\frac{1}{2}V_{\text{C}}(\vec{r}) + \epsilon_{\text{xc}}(\vec{r})\rho(\vec{r}) - V_{\text{xc}}(\vec{r})\right]\mathrm{d}\vec{r} \end{aligned} \tag{3}$$

where the total electron density is

$$\rho(\vec{r}) = \sum_{i=1}^{\mathrm{occ}} |\psi_i(\vec{r})|^2. \tag{4}$$

For the exchange–correlation potential we use in the present study the approximate form of von Barth and Hedin [28].

We study systems like those of figure 1, i.e., systems with only one type of atoms (figure 1(a)) or with two types of atoms (figures 1(b)–1(d)). In figure 1(b) one of the atoms is assumed to be deposited outside the other one, which almost exclusively is the experimentally realized situation, whereas in figure 1(c) we consider the case where one metal forms a shell within the other one (this can thus be considered a special case of a nanoparticle containing three concentric layers of different metals). Finally, figure 1(d) represents a homogeneous alloy of the two metals.

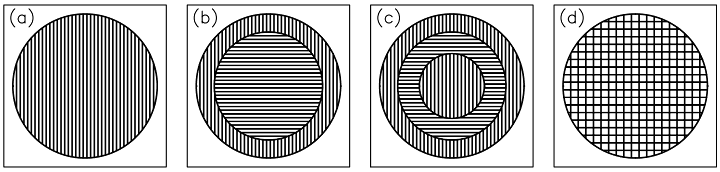

Figure 1. A schematic representation of the different clusters studied in the present work. The horizontally hatched regions correspond to one type of metal atoms and the vertically hatched regions to another type. The system of (a) contains only one type of atoms, whereas those of (b) and (c) contain two types of atoms that occupy different parts of the system. Finally, the two metals are completely mixed for the system of (d).

For each metal separately we use the jellium density as it would be for the infinite, pure, crystalline material. For the alloy of figure 1(d) the density was chosen such that the same total volume as that of the separated materials was obtained. With N_e being the number of valence electrons per atom, ρ_s the jellium density, and r_s the electron-gas parameter (the radius of a sphere containing one elementary charge of the jellium), we used the values of table 1. Since the 3d electrons of Cu and Ni are well localized to the atomic cores, we have chosen to include these in the jellium model, although it can be discussed whether this a reasonable approximation, and whether N_e equals 1 and 2 for the two elements, respectively. Similarly, for Au and Cd we have included the 5d and 4d electrons in the valence electrons, since these orbitals are considerably less localized to the core regions. But also this may be questioned. On the other hand, for the sake of identifying general trends of the electronic properties of larger bimetallic clusters we consider these approximations justified.

Table 1. The number of valence electrons per atom N_e, the jellium density ρ_s, and the electron-gas parameter r_s for the different elements of the present study. The length scale is au.

Atom	N_e	ρ_s	r_s
Cu	1	0.012585	2.667
Ni	2	0.027190	2.063
Cd	10	0.068656	1.5150
Au	11	0.096096	1.3544

Before proceeding to the results of our study we recall one weakness of the simplest jellium model. For an infinite, homogeneous system, characterized by the jellium density ρ_s or the electron-gas parameter r_s, the total energy per electron is the sum of the kinetic energy and the exchange–correlation energy. Since the occupied electronic orbitals are free-electron-like with k up to the Fermi momentum

$$k_{\mathrm{F}} = \left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}$$

the kinetic energy per electron is

$$e_{\mathrm{k}} = \frac{3}{10}\left(\frac{9\pi}{4}\right)^{2/3}\frac{\hbar^2}{m}r_s^{-2} \tag{5}$$

whereas the exchange–correlation energy per electron is

$$e_{\mathrm{xc}} = \epsilon_{\mathrm{xc}}[\rho_s]. \tag{6}$$

In figure 2 we show these as well as their sum as a function of ρ_s or r_s. In particular we see that the total energy is upward curved, so any alloy will have a lower total energy than the two separate systems. We will expect this tendency to show up also for the finite systems of this work. Moreover, there is an optimal, universal jellium density, which might imply that as large parts as possible of any system would strive towards that density. We add that there are approaches that cure this weakness of the simplest jellium model, including the stabilized-jellium method of Perdew *et al* [29], but we have not used these here.

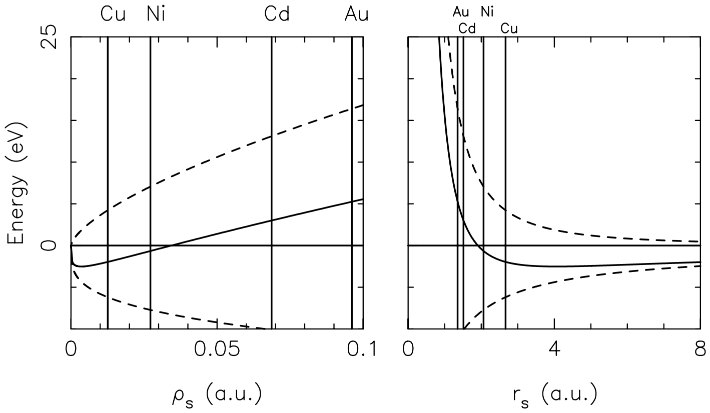

Figure 2. Kinetic energy per particle (upper dashed curve), exchange–correlation energy per particle (lower dashed curve), and total energy per particle (solid curve) for the infinite, homogeneous jellium as functions of (a) ρ_s and (b) r_s. The vertical lines mark the values for the metals of the present work.

3. Ni + Cu

In a first set of calculations we studied clusters consisting of a fixed number ($N_{\mathrm{Ni}} = 100$) of Ni atoms and a variable number ($17 \leqslant N_{\mathrm{Cu}} \leqslant 226$) of Cu atoms. Thereby we considered the two types of structure of figures 1(b) and 1(c). For clusters consisting of only one type of atoms (figure 1(a)) it has been found that, as a function of the radii R of the jellium, particularly stable clusters are found for clusters whose radii differ by

$$\Delta R \simeq 0.603\, r_s \tag{7}$$

(see, e.g., [7]) which can be explained through the theory of Balian and Bloch [30]. Actually, in our recent work on Cs clusters [9] we found similar results not only within the jellium model but also for a tight-binding model.

For the Ni + Cu clusters the natural question arises of whether similar particularly stable clusters are found and, in that case, whether there is any regularity in their occurrence similar to that of equation (7). In order to address this question we proceed as follows.

For each of the two types of system of figures 1(b) and 1(c) we considered both the case where the horizontally hatched regions correspond to Ni atoms and the case where these regions represent Cu atoms. This gives in total four sets of calculations. The complete set of total energies E_{tot} was subsequently approximated through

$$E_{\text{tot}} \approx \tilde{E}_{\text{tot}} = v_{\text{Ni}} V_{\text{Ni}} + v_{\text{Cu}} V_{\text{Cu}} + a_{\text{CuNi}} A_{\text{CuNi}} + a_{\text{Ni}} A_{\text{Ni}} + a_{\text{Cu}} A_{\text{Cu}} \tag{8}$$

where the a and v are constants that are determined through a least-squares fit, and where V_{Cu} and V_{Ni} are the volumes of the Cu and Ni parts of the cluster, respectively, A_{Cu} and A_{Ni} are the surface areas of the Cu parts and the Ni parts, respectively (for all systems one or the other vanishes), and A_{CuNi} is the total area of the Cu–Ni interfaces. Subsequently, we defined the excess energy:

$$E_{\text{excess}} = E_{\text{tot}} - \tilde{E}_{\text{tot}}. \tag{9}$$

The radius of any cluster is given by

$$R = \left[N_{\text{Cu}} r_s^3(\text{Cu}) + 2N_{\text{Ni}} r_s^3(\text{Ni})\right]^{1/3} \tag{10}$$

and in figure 3 we show the excess energy for the different clusters as functions of the radius R. Simultaneously, we have marked R for which

$$R = n \times 0.603\, r_s \tag{11}$$

with n being an integer. Here, we considered different values of r_s, i.e., either the value for Ni (dashed lines), that for Cu (dot–dashed lines), or an average $r_s(\text{av})$ (solid lines) defined through

$$R = [N_{\text{Cu}} + 2N_{\text{Ni}}]^{1/3} r_s(\text{av}). \tag{12}$$

(That is, $r_s(\text{av})$ is not a constant, but size dependent.)

In figure 3 we observe that the excess energy is much more negative in figures 3(a) and 3(d) than in figures 3(b) and 3(c). These are the systems for which the radial extents of the Cu regions are the largest and, therefore, we consider this result a consequence of the present jellium model that predicts Cu to be more stable than Ni (cf. figure 2). The differences in the radial extent can, e.g., be quantified by considering clusters of 200 Ni atoms and 400 Cu atoms. For those of figure 2(b), the Cu atoms cover a radial range of 19.65 au when they form the inner part, but only 7.11 au when they form the outer part. Simultaneously, the Ni atoms cover radial ranges of 2.66 and 15.20 au, respectively. For the systems of figure 2(c) of the same size, the thickness of the Cu layer is 9.00 au, when being sandwiched between the Ni regions (whose thicknesses are 12.06 and 1.24 au), whereas the opposite system has a Ni-layer thickness of 3.81 au and Cu-layer thicknesses of 15.60 and 3.90 au.

In figure 3 we also see that there are systems that are particularly stable. These correspond to $R = 15.185$ and 17.292 au in figure 3(a), 14.674, 15.401, and 18.100 au in figure 3(b), 13.997, 15.185, and 17.292 au in figure 3(c), and 12.877, 15.401, and 17.035 au in figure 3(d), or to $N_{\text{Cu}} = 92$ and 180; 74, 100, and 220; 52, 92, and 180; and 20, 100, and 168 for the four cases, respectively. The similarity of those numbers for the different systems is striking. On the other hand, neither those values of N_{Cu} nor those of the total number of electrons $N_{\text{Cu}} + 2N_{\text{Ni}}$ for which particularly stable structures occur are close to the magic numbers observed for the jellium model of a single metal (see, e.g., [9]). Thus, the two-component clusters have properties different from those of the one-component clusters, also within the simple jellium model.

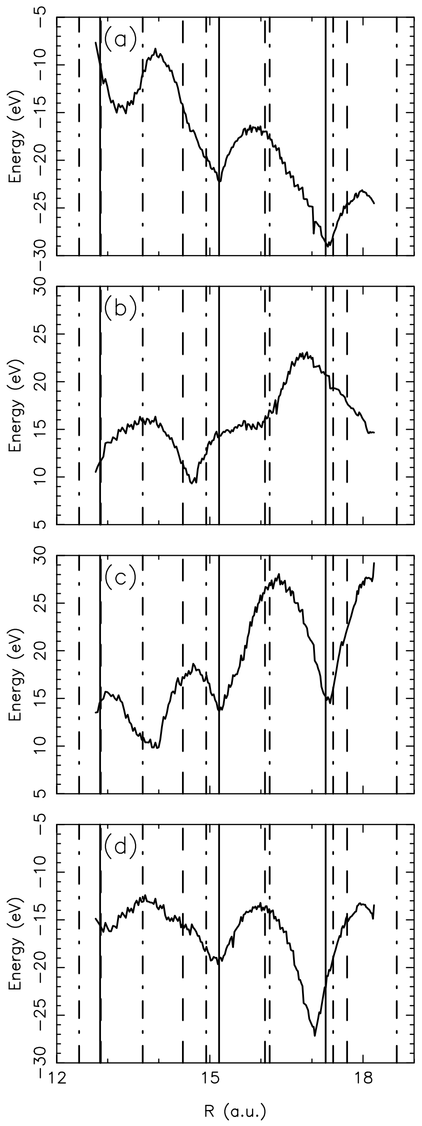

Figure 3. The excess energy of equation (9) as a function of the radius of the cluster for Ni + Cu clusters. The systems of (a) and (b) correspond to figure 1(b), whereas those of (c) and (d) correspond to that of figure 1(c). In (a) and (c), the vertically hatched regions in figure 1 represent Ni atoms, whereas in (b) and (d) they represent Cu atoms. Finally, the vertical lines correspond to equation (11) for different values of r_s (for details, see the text).

This is confirmed by the attempts to identify a regularity in the particularly stable clusters in figure 3. Here, r_s (av) is seen to be that quantity that most closely correlates with the minima in the excess energy, although there are system-specific differences (e.g., for that of figure 3(b)), and size-specific ones (e.g., for the smallest clusters). We mention that also Ekardt [21] in his jellium study of considerably smaller systems found that some of the properties depend critically on the precise structure of the two-component system and not only on the total number of electrons.

Finally, the fit of equation (8) gave

$$\begin{aligned} v_{\mathrm{Ni}} &= -0.00735 \\ v_{\mathrm{Cu}} &= -0.01964 \\ a_{\mathrm{CuNi}} &= -0.00477 \\ a_{\mathrm{Ni}} &= -0.04205 \\ a_{\mathrm{Cu}} &= -0.04058 \end{aligned} \tag{13}$$

with energies in eV and lengths in Bohr. Here, v_{Ni} and v_{Cu} correspond to -0.27 and -1.56 eV per electron, respectively, in fair agreement with the values for the infinite systems; cf. figure 2.

In order to obtain further insight into this class of systems we considered the nine systems whose electron and background densities are shown in figure 4. For an infinite, homogeneous system, the introduction of a surface will lead to the well-known Friedel oscillations of the

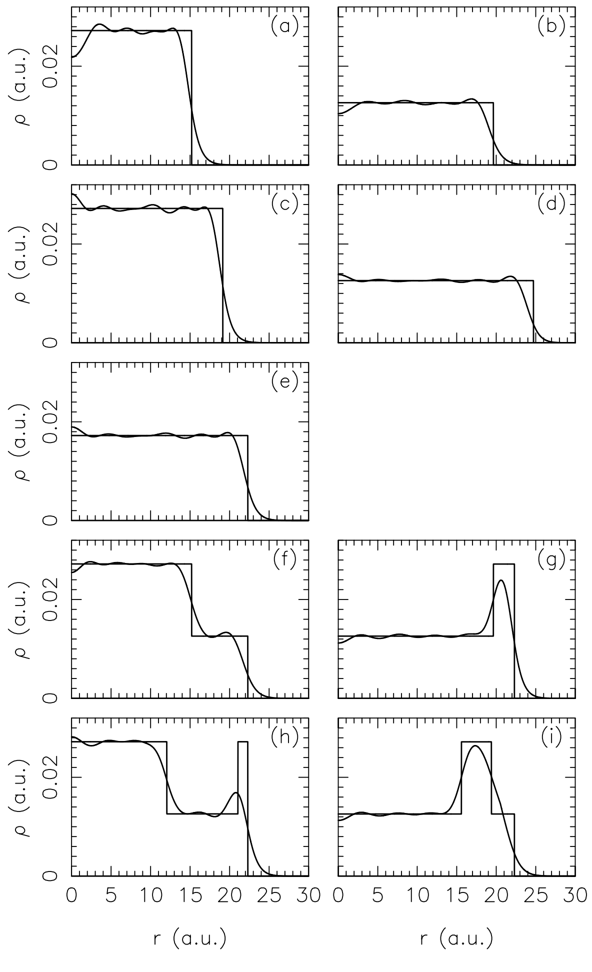

Figure 4. Radial electron and background density for systems with (a) 200 Ni atoms, (b) 400 Cu atoms, (c) 400 Ni atoms, (d) 800 Cu atoms, and (e)–(i) 200 Ni + 400 Cu atoms. The systems of (a)–(d) correspond to figure 1(a), that of (e) to figure 1(d), those of (f) and (g) to figure 1(b), and those of (h) and (i) to figure 1(c). Since Ni has the larger background density, the Ni regions are readily identified.

electron density with a wavelength of 1.636 r_s [31]. Also for the finite, spherically symmetric cluster, the presence of the surface will lead to such oscillations, although with a somewhat more complex form [32]. They are recognized for the homogeneous systems of figures 4(a)–4(e), and for the other systems, in figures 4(f)–4(i), it is seen that in those regions, that are so large that the oscillations can develop, the wavelength is largely determined by the specific material with, however, some system-specific modifications.

The finding that the stability is determined mainly by the complete system and not by the individual components can be understood from figure 5, which shows the single-particle potential together with the orbital energies. It is seen that, except for the absolutely deepest orbitals, all (unoccupied and occupied) orbitals are spread out over the complete system.

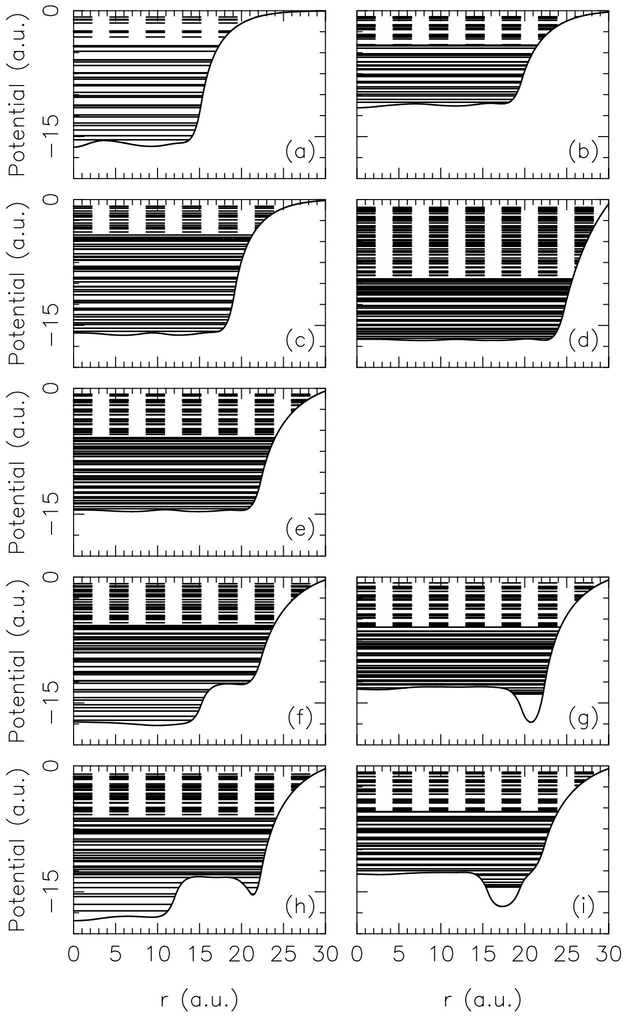

Figure 5. The single-particle potential and the single-particle energies (solid lines for occupied orbitals and dashed lines for unoccupied ones) for the same systems as in figure 4.

The density of states—figure 6—shows a large similarity with that of a homogeneous electron gas, except for being split into individual peaks due to the finite size of the systems of the present study. Furthermore, a careful inspection reveals that each curve can be decomposed

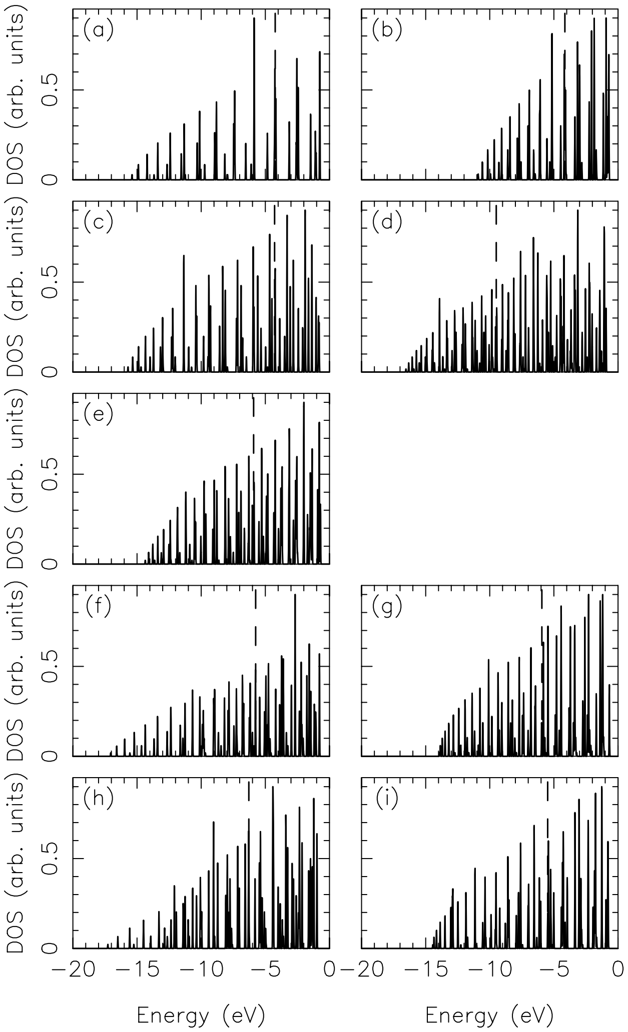

Figure 6. The densities of states for the same systems as in figure 4. The vertical dashed lines separate occupied and unoccupied orbitals. The curves do not have the same ordinate scales.

into different ones, each having the characteristic $\sqrt{\epsilon}$-behaviour of the homogeneous electron gas, but displaced relatively to each other. Each of these corresponds to a different quantum number n, describing the number of radial nodes for the individual orbitals.

4. Au + Cd

As mentioned in the Introduction, Schmid *et al* [19] have found that bimetallic colloids consisting of Au and Pd possess catalytic activities that depend on the size of the colloidal particles. In particular they found that the catalytic activity of pure Pd colloids was significantly smaller than that of colloids consisting of a Au core covered with Pd atoms. For the latter they found, moreover, that the activity increased with decreasing size of the colloids which may be a consequence of the increased surface-to-volume ratio.

The particles of their study are somewhat larger than those we can treat (i.e., their colloids have radii of ~200 au). Moreover, the frontier orbitals of Pd are partly due to 4d functions and partly due to 5s functions, which, however, appear at quite different energies, so the simplest jellium model may be too inaccurate. This orbital-energy difference is reduced significantly for Cd (in density-functional calculations on the isolated atoms we found 4d levels at −12.4 and −7.4 eV for Pd and Cd, respectively, and 5s levels at −6.4 and −5.1 eV). Therefore, we shall here replace Pd by Cd and accordingly study Au–Cd bimetallic colloids with special emphasis on catalytic properties.

As a simplification, a heterogeneous catalytic process can be separated into three steps. The first step involves the adsorption of the educts on the surface of the catalyst (e.g., through the creation of chemical bonds between catalyst and educts). In the second step, the educts interact on the catalyst forming the products, and in the third step the products are desorbed from the catalyst. Each step is complex and depends sensitively on microscopic details of the catalyst and the educts/products. In particular the structure, including the existence of defects, of the catalyst as well as surface states of the catalyst may play dominating roles. None of these is described very accurately with the present jellium model. On the other hand, the model may be able to identify overall size dependences of the catalytic properties of these colloids.

First we considered clusters containing 10, 100, or 1000 Cd atoms, and subsequently we studied clusters consisting of $N_{\mathrm{Au}} = 200$ Au atoms covered by N_{Cd} atoms with N_{Cd} lying in the ranges 70–600 or 1000–1220 or being 0 (70 is roughly the number of Cd atoms that are needed to cover the Au_{200} nanoparticle). The total energy per valence electron:

$$E_{\mathrm{rel}} = E_{\mathrm{tot}}/(11N_{\mathrm{Au}} + 10N_{\mathrm{Cd}}) \tag{14}$$

for the Cd-covered Au clusters is—cf. figure 7(a)—a smooth function of the radius of the cluster, R. On fitting this function with

$$\tilde{E}_{\mathrm{rel}} = a + bR^{-3} + cR^{-1} \tag{15}$$

and subsequently studying

$$\Delta E_{\mathrm{rel}} = E_{\mathrm{rel}} - \tilde{E}_{\mathrm{rel}} \tag{16}$$

we obtain the results of figure 7(b). These show oscillations with a fairly constant periodicity close to 1 au (i.e., close to 0.603 r_s) as might be expected from the discussion of the previous section.

Also the Fermi level—figure 7(c)—shows an oscillatory behaviour that furthermore correlates very well with that of the relative total energy of figure 7(b). Moreover, the Fermi energy of these clusters is in general lower than that of the pure Cd clusters without the Au core.

In the first step of the catalytic reactions when the educts interact with the catalyst, the strengths of these interactions are, using perturbation theory as giving a first estimate, determined by the energy difference between the frontier orbitals of the catalyst and the educts. Thus, the size-dependent oscillations in figure 7(c) suggest that these interactions will also depend oscillatorily on the size of the colloidal catalyst. Thus, the size-dependent catalytic activities observed by Schmid *et al* [19] may very well originate from these oscillations, although their colloids were not so monodisperse that the details of the oscillations of figure 7 could be resolved. Moreover, the overall shift of the Fermi level compared with the pure Cd clusters may also explain their observation of a higher catalytic activity of Cd colloids with an Au core compared with that of pure Cd colloids.

Finally, in figure 8 we show the densities of states for various Au, Cd, and Au+Cd clusters as functions of their size. Compared with the systems of figure 6 these contain considerably more electrons, but, nonetheless, the conclusions drawn above remain essentially unaltered.

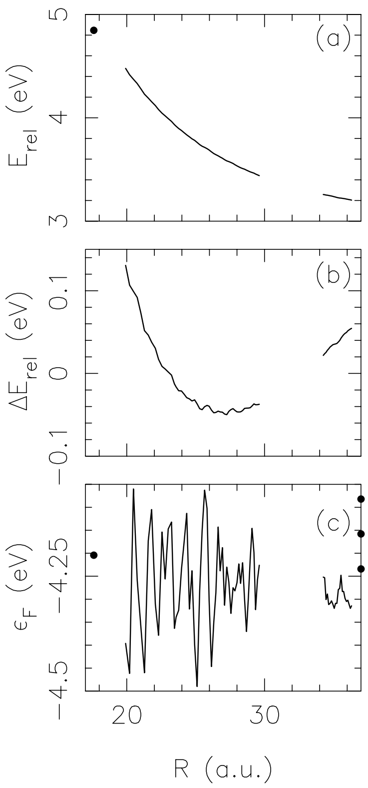

Figure 7. (a) The total energy per electron for the Au–Cd bimetallic clusters. The solid point to the left marks the value for the uncovered Au cluster. (b) As (a), but for the quantity ΔE_{rel} of equation (16). (c) As (a), but for the Fermi energy. Here, the solid points on the right-hand border mark the values for the pure Cd clusters of 10 (uppermost point), 100, and 1000 (lowest point) atoms.

5. Conclusions

In this paper we have applied the (spherical) jellium model in studying colloids or clusters containing two types of metal atoms. Compared with the systems containing only one type of atoms the present systems are seen to possess very similar properties. In particular, almost all valence orbitals are spread out over the complete system and, in consequence, the regularity with which the radius of particularly stable clusters occurs is dictated by an average electron density.

Moreover, we found that the Fermi energy as a function of system size shows an oscillatory behaviour that correlates very well with that of the total energy, but also that, for the present system, it is overall lower than that of the pure clusters. Both findings might explain the experimental results on catalytic activities of Pd/Au bimetallic colloids.

Finally, we stress again that the jellium model can be considered only a first approximation. It suffers from various weaknesses of which we stressed some in the present work. These include also that the metals of the present study, Ni, Cu, Cd, and Au, may not be very well described within this model. On the other hand, due to its simplicity it may be able to catch some of the dominating physical properties of the systems of interest that due to the complexity of these systems are out of reach with more exact theoretical methods.

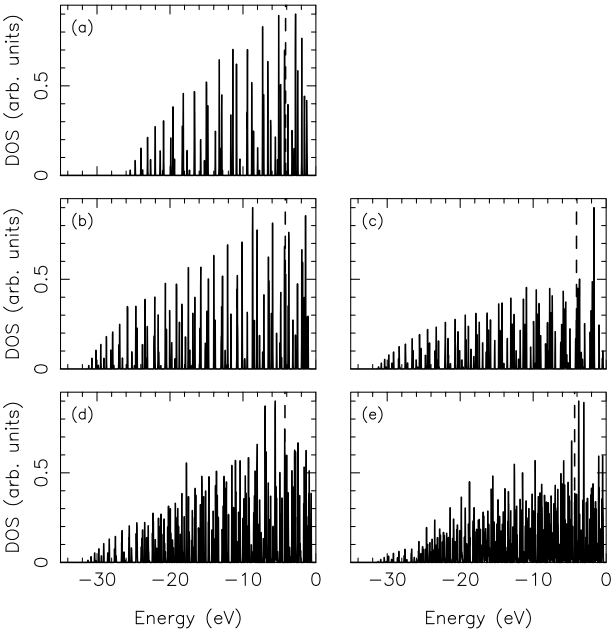

Figure 8. As figure 6, but the for Au–Cd clusters. (a) shows the density of states for the cluster with 100 Cd atoms, whereas (b)–(e) correspond to clusters with 200 Au atoms covered with (b) 0, (c) 90, (d) 395, and (e) 1220 Cd atoms. The curves do not have the same ordinate scales.

Acknowledgments

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