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A simple semiclassical model for ionic structure effects in large metal clusters *

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A semiclassical version of the density functional approach is used to investigate the structure of metal clusters. The effect of the ionic structure is included in a schematical way, assuming that the ions are distributed on concentric shells. The method, which allows a simultaneous investigation of geometrical and electronic effects, is computationally very simple and can be extended up to very large cluster sizes. Predictions of this model in the medium size range are compared with the results of available microscopic calculations, yielding a very good agreement.

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1. Introduction

In spite of the success of the *spherical jellium model* (SJM) in describing metal clusters, its total neglect of the ionic structure is obviously a serious drawback. Not only the electronic orbitals predicted by the SJM differ in some cases from the observed ones, but also the average behaviour of properties like ionization potentials and static dipole polarizabilities are often not reproduced satisfactorily [1]. It is therefore desirable to go beyond the SJM, which only accounts for electronic shell effects, by including to some extent the effect of the ionic structure. Theoretical calculations along this line have been performed in the small size range, in which 3-dimensional ab-initio calculations are still possible [2], and in the medium size range ($N \leqq 50$), where drastic approximations are already needed [3]. In [3], Iñiguez et al. use a *density functional approach* in which the total energy is also minimized with respect to the ionic coordinates. The Coulomb energy between the point-like ions is treated exactly, while the ionic potential acting on the electrons is replaced by its spherical average. (This approximation is equivalent to imposing a spherical symmetry on the electron density.) Since the computational difficulties of this procedure increase as the cluster size grows, this method cannot be extended to very large clusters.

The purpose of the present work is to develop an alternative method that permits to investigate simultaneously electronic and structural effects in the large cluster limit (and, eventually, to gain more insight into the transition between cluster and bulk metal). As in [4] we use a semiclassical *density variational approach*, making use of the *extended Thomas Fermi* (ETF) *model* for the kinetic energy and parametrizing the electron density profile. This model, which puts no limitations to the size of the clusters, provides results in very good agreement with the averaged results of corresponding microscopic Kohn-Sham calculations, when applied in the framework of the SJM [4]. The new ingredient of the present work is the inclusion of the ionic structure. Like in [3], spherical symmetry is imposed on the cluster. As a further simplification, the discrete point-like distribution of the ions will be replaced by a continuous distribution, so that the number of variational parameters corresponding to the ions is drastically reduced. Of course, the structural effects are thereby included only in a schematical way. But the main advantage of our approach is its computational simplicity which allows calculations in a size range where other methods become prohibitive.

2. The model

The ground state energy of a neutral cluster with a given configuration of the ions is written as a functional of the local electron density $\rho(\mathbf{r})$ (normalized to the number of valence electrons):

$$E[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int \mathrm{d}\mathbf{r}\,V_I(\mathbf{r})\,\rho(\mathbf{r}) + E_I\,. \tag{1}$$

Here T is the kinetic energy in the ETF approximation up to fourth-order gradient corrections and E_{xc} the ex-

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change-correlation energy for which we use the LDA functional of Gunnarsson and Lundqvist [5]. The third term is the electronic Hartree energy, and V_I and E_I are the potential and the electrostatic energy of the ions, respectively. In the present work we focus on the treatment of these last two terms for which we introduce a drastic approximation (less drastic, however, than the jellium approximation!). The ions are represented by pseudopotentials, for which we use Ashcroft's form [6]. Furthermore, in an analogous way as done in metal surface calculations [7, 8], where the positive charges are smeared out over each lattice plane, we replace the point-like ion distribution by a continuous distribution consisting of a fixed number of uniformly charged spherical shells. This assumption is supported by Manninen's work [9] which shows that relaxed spherical ionic structures lead to more stable clusters than crystalline ones. This is also in the spirit of the calculation by Iñiguez et al. [3] which indicates that the ions are evenly distributed on a few shells. Therefore, we replace the total ionic potential

$$V_I(\mathbf{r}) = \sum_{i=1}^{N} v_i^{ps}(|\mathbf{r}-\mathbf{R}_i|, r_c), \tag{2}$$

where v_i^{ps} are the individual ionic pseudopotentials with empty-core radius r_c [6], by the continuous potential

$$\tilde{V}_I(\mathbf{r}) = \sum_{j=1}^{n} \tilde{v}_j^{ps}(|\mathbf{r}-\mathbf{R}_j|, r_c) \tag{3}$$

with

$$\tilde{v}_j^{ps}(|\mathbf{r}-\mathbf{R}_j|, r_c) = \frac{4\pi R_j^2 \sigma_j}{R_j} - \delta v_j(R_j, \sigma_j, r_c, r) \quad r \leqq R_j$$
$$= \frac{4\pi R_j^2 \sigma_j}{r} - \delta v_j(R_j, \sigma_j, r_c, r) \quad r > R_j \tag{4}$$

and

$$\delta v_j(R_j, \sigma_j, r_c, r) = \frac{2\pi R_j \sigma_j}{r} (r_c - |R_j - r|)\, \Theta(r_c - |R_j - r|). \tag{5}$$

The radii R_j and the surface charge densities σ_j of the shells are variational parameters. In (3), n is the total number of shells. If we set $n = N$ (i.e. as many shells as ions), the approximation (3) is equivalent to performing a spherical average of V_I as in [3]. Since according to [3], the ions seem to distribute themselves on a few shells ($n \leqq 2$ for $N \leqq 40$), we will take $n \ll N$, restricting in this way the variational space for (R_j, σ_j). As a criterion to fix n we require that the minimization procedure with $(n+1)$ shells gives identical results to those obtained with n shells.

The electrostatic energy of the ions E_I can be decomposed into:

$$E_I = \sum_{j<k}^{n} \frac{N_j N_k}{R_k} + \sum_{j=1}^{n} E_{jj}(N_j, R_j). \tag{6}$$

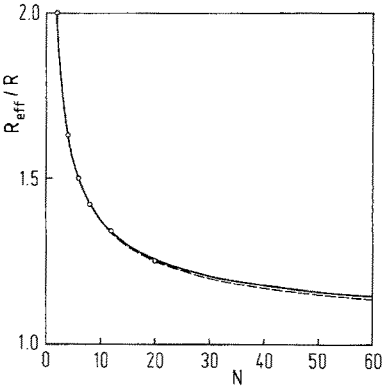

Fig. 1. Ratio R_{eff}/R as a function of the number of atoms in the shell, see (7). The analytical values for $N = 2, 4, 6, 8, 12, 20$ are indicated by dots. The full line corresponds to parametrization $P1$ ($W_1 = 1.04$, $W_2 = 0.592$, $W_3 = -0.664$, $W_4 = 0.890$), the dashed line to parametrization $P2$ ($W_1 = 0.832$, $W_2 = 2.00$, $W_3 = -3.81$, $W_4 = 3.03$)

The first term gives the interaction energy among different shells of charge $N_j = 4\pi\sigma_j R_j^2$. This is a good approximation to the energy of the discrete distribution if the point-like charges are evenly distributed on the shells. The second term, which is the sum of the self-energies of each shell, has to be evaluated with some care in order to avoid an overestimation of the ion-ion repulsion. It is easy to see that the energy of point-like charges uniformly distributed on a sphere is lower than the self-energy of a uniformly charged shell of same radius and charge. Therefore we approximate the energy of N ions, distributed on a sphere of radius R, by:

$$E_{jj}(N, R) = \frac{N(N-1)}{2R_{eff}(N, R)}, \tag{7}$$

where R_{eff} is the effective radius of the shell. It is clear that R_{eff}/R is a decreasing function of N, which takes the value $R_{eff}/R = 2$ for $N = 2$, and $R_{eff}/R = 1$ for $N \to \infty$. In order to estimate this quantity as a function of N, we have calculated analytically the Coulomb energy of the energetically most favorable distributions for $N = 4$, 6, 8, 12, 20 (i.e., for the regular polyhedrons), and evaluated R_{eff}/R for these values of N. We have then parametrized $R_{eff}(N, R)$ in the form:

$$R_{eff}(N, R) = R\left\{1 + \sum_{l=1}^{4} W_l N^{-l/2}\right\} \tag{8}$$

and tried different sets of parameters W_l. In Fig. 1, we present the results for two parameter sets ($P1$ and $P2$) which fit the calculated values of R_{eff} and have the right behaviour for $N \to \infty$. Of course, in order to have a good parametrization for all values of N, the analytical calculation of the Coulomb energy of the point-like distribution should be also performed for some larger systems. Work along this line is being persued.

3. Results

We first use the continuous approximation for the ion distribution ((3) to (5)) to derive a "universal" cluster geometry, following the procedure proposed by Manninen [9]. The approximate Madelung energy (which includes most of the structural dependence)

$$E_{\mathrm{Mad}} = E_I + \int \mathrm{d}\,\mathbf{r}\, V_I(\mathbf{r})\, \rho_0(\mathbf{r}) \tag{9}$$

is minimized with respect to the ionic parameters (R_j, σ_j). Here, $\rho_0(\mathbf{r})$ is a reference spherical electron density given by a step function. It only gives a scaling factor since the quantities R_j/R_0 (R_0 being the cluster radius) and N_j depend only on the ion number N. In Fig. 2 we show the population of the different shells as a function of the cluster size obtained with the parameter sets $P1$ and $P2$ for $R_{\mathrm{eff}}(N, R)$ in (8). In Fig. 3 we compare our results in the medium size range to those obtained in [9] using a point-like distribution for the ions. We observe that, except for the obvious fact that our shell populations are not discrete, the restructuration mechanism for increasing Z

$$\ldots (n \text{ shells}) \rightarrow (n \text{ shells} + 1 \text{ central atom}) \rightarrow ((n+1) \text{ shells}) \ldots$$

is very well reproduced. However, the quantitative agreement with [9] in Fig. 3 depends on $R_{\mathrm{eff}}(N, R)$. Indeed, the results obtained using $P1$ and $P2$ differ by approximatively 10%.

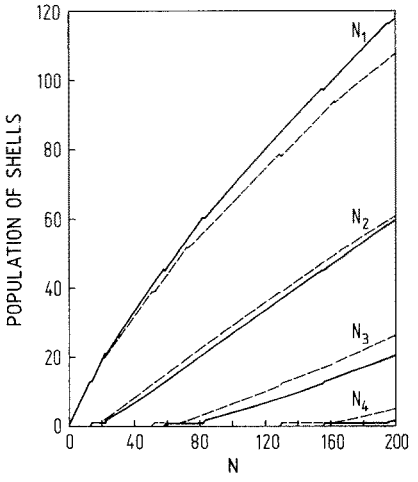

Fig. 2. Population of the different shells for "universal" cluster structures as a function of the cluster size, calculated using a continuous distribution for the ions. The full line corresponds to parametrization $P1$, the dashed line to parametrization $P2$

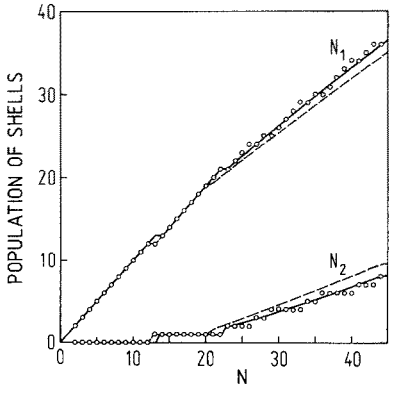

Fig. 3. As in Fig. 2, medium size range. The dots indicate the results of [9], using a point-like distribution for the ions

Table 1. Radii R_1 and R_2 (in a.u.), charges N_1 ($N_2 = N - N_1$) of the ionic shells, and central electronic density ρ_e, obtained by a minimization of the approximate Madelung energy (AM), by a minimization of the total energy using two different parametrizations (SD and FD), and by the microscopical calculation of [3] (SAPS). See text for details. ρ_s is the bulk density used as an input in AM

	AM	SD	FD	SAPS
Na_{25}				
R_1	2.8	2.9	3.4	3.5
R_2	8.8	8.9	8.9	9.0
N_1	2.4	2.4	3.7	3.0
ρ_e	($\rho_s = 0.00384$)	0.00380	0.00461	
Na_{30}				
R_1	3.7	3.7	4.2	4.0
R_2	9.6	9.6	9.5	9.5
N_1	3.8	3.8	5.5	4.0
ρ_e	($\rho_s = 0.00384$)	0.00380	0.00475	
Mg_{25}				
R_1	2.4	2.7	3.3	3.2
R_2	7.4	8.3	8.3	8.0
N_1	2.4	2.4	3.4	3.0
ρ_e	($\rho_s = 0.0128$)	0.00932	0.01047	
Al_{18}				
R_1	1 central ion	1 central ion	1 central ion	1 central ion
R_2	5.8	5.3	5.2	5.5
N_1	1.0	1.0	1.0	1.0
ρ_e	($\rho_s = 0.0269$)	0.0347	0.0371	

We want to stress again the simplicity of our method which permits to extend the calculation up to a size range for which other calculations become prohibitive. The configurations shown in Fig. 2 are obtained by means of a minimization with respect to at most 7 variational parameters. In order to go to very large clusters containing thousands of atoms, one should still reduce the number of parameters by observing some regularities in the behaviour of R_j and σ_j. For instance, we noticed that the surface charge density of the shells is approximatively constant as a function of N: $\sigma_j r_s^2 = 0.35 \pm 0.03$, r_s being the Wigner-Seitz radius of the corresponding metal. Such properties should be investigated in order to understand the transition from cluster to the bulk metal. The radii of the shells obtained by this procedure using the set $P1$ are shown (AM) for some particular cases in Table 1. We fix ρ_0 to the bulk density of the corresponding metal: $\rho_0 = \rho_s = 3/(4\pi r_s^3)$.

In Table 1, we also present the results of the full minimization (using P_1) of the total energy (1) with respect

to both ionic and electronic parameters. For the spherical electron density in our variational ETF calculation we use two different trial functions. (SD): a simple step function $\rho(r)=\rho_e\,\Theta(R_e-r)$ with just one variational parameter ρ_e, and (FD): an asymmetric Fermi function $\rho(r)=\rho_e/(1+\exp(r-R_e)/\alpha)^\gamma$ with three variational parameters. In the last column, we show for comparison the results obtained in a microscopic Kohn-Sham calculation (SAPS) with a discrete distribution for the ions and the spherical average of the ionic potential [3]. The empty core radii r_c for Na, Mg and Al are 1.74, 1.50 and 0.97 a.u., respectively.[1]

All the models, including the very simple AM, predict a 2-shell structure for Na_{25}, Na_{30}, Mg_{25}, and one shell plus one central atom for Al_{18}. Moreover, the radii of the shells R_1 and R_2 and their charges N_1 and N_2 are in good agreement with the values obtained in the microscopical SAPS calculations [3].

Concerning the electronic density ρ_e, we observe that the one resulting from the full minimization with the step function parametrization (SD) is approximatively equal to the bulk density ρ_s in the case of $Na_{25,30}$, while it is lower than ρ_s (by 25%) for Mg_{25} and higher for Al_{18}. Although this should only be taken as a qualitative feature, since the SD parametrization does not allow for surface effects, it is still an indication that changes in the cluster volume will occur (when compared with the predictions of the jellium model), affecting the values of ionization potentials and polarizabilities.

The electron density profiles derived with the FD parametrization show a higher central density and a larger diffuseness than the profiles obtained in an analogous variational ETF calculation using the jellium model. For instance, for Na_{30} we have: $\rho_e=0.00475$, $\alpha=1.20$, $\gamma=1.40$ compared with $\rho_e^{jm}=0.00398$, $\alpha^{jm}=0.53$ and $\gamma^{jm}=0.55$. These profiles are shown in Fig. 4. Consistently, we observe that in the FD calculation the ions tend to concentrate more towards the inner shell than in the other calculations. Nevertheless, the fact that $N_1^{FD}>N_1^{SAPS}$ should not be taken too seriously since the parametrization FD, which works very well in the jellium model [4], is not flexible enough if one includes the ionic geometry, at least for small clusters. This can be seen in Fig. 4, where together with the jellium model and FD electronic profiles, we show the profile resulting from the Kohn-Sham calculation with the same ionic geometry. The FD profile reproduces well the surface and the density tail, but of course cannot account for the oscillations due to the presence of the shells. This is an indication that a more flexible parametrization is needed in the small and medium size range. An alternative procedure would be to first determine the ion geometry by performing a semiclassical calculation and finally perform a Kohn-Sham calculation with fixed positions of the shells. Anyway, the electron density will become smoother as the cluster size increases and we expect the FD parametrization to be good enough in the large size range.

[1] These values, which differ slightly from those used in [6–8], were adjusted to fit atomic ionization potentials in [3]

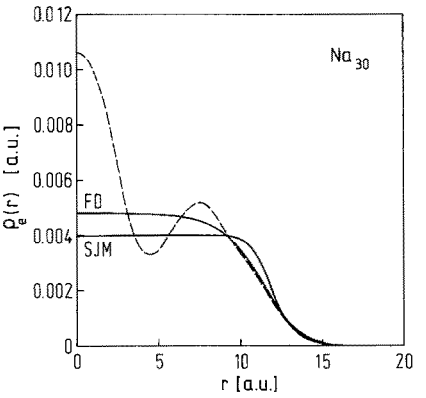

Fig. 4. Electron density profiles for Na_{30} clusters, calculated in the present model (FD) and in the jellium model (SJM). The corresponding ionic parameters, obtained self-consistently in the FD calculation, are $R_1=4.2$, $R_2=9.5$ and $N_1=5.5$. The dashed line shows the result of a Kohn-Sham calculation with the same ionic parameters as in FD (kept fixed)

These few examples were presented here to show the reliability of our simple model in the medium size range, where microscopical results are still available. A systematical calculation of cluster structures in the large size range will be presented in a subsequent article.

4. Summary and conclusion

We have generalized the semiclassical density variational method for the description of metal clusters by including the effect of the ionic structure. This is done in a schematical way, assuming that the ions are evenly distributed over a small number of spherical shells. The number of shells is fixed by the requirement that the addition of a new shell should not modify the results of the minimization. Another crucial approximation, which has to be investigated in more detail, concerns the estimation of the Coulomb self-energy of each shell when replacing the discrete distribution by a continuous one.

Our method has been applied in the medium size range, where its predictions can be compared with more realistic (but less simple) models. The cluster structures obtained by minimizing the approximated Madelung energy within our model are found in good agreement with the ones obtained using a point-like distribution for the ions. Also, our results of the full minimization with respect to ionic and electronic parameters reproduce well the results of a microscopic Kohn-Sham calculation, except for the electron density profile which cannot be described with our smooth parametrization.

The approximations involved in the present model become more justified as the cluster size increases. This, together with its computational simplicity, might make our approach very useful for the description of very large clusters. A systematical calculation of ionization potentials and dipole polarizabilities in the large size range will be presented in a forthcoming publication.

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Note added in proof. The analytical Coulomb self energy of the ions has meanwhile been calculated for two more cases, namely $N=32$ (superimposed dodecahedron and icosahedron) and $N=60$ (the Fullerene 'soccer ball'). The results for R_{eff}/R lie very close to the solid curve on Fig. 1, thus confirming the use of the parametrization $P1$.