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Self-consistent Sommerfeld droplet as a simple model for an accurate prediction of the electronic properties of small metal particles

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The combination of the self-consistent jellium model of solid-state physics and the distorted droplet model of nuclear physics is shown to provide an excellent working scheme for an accurate prediction of the electronic properties of small particles of the *sp*-bonded metals. The model is parameter-free and relies on the experimentally confirmed fact that the mean ionic volume of these clusters is nearly size independent.

Beginning with the early work by Martins, Car and Buttet[1] there is a great variety of literature concerning the application of the spherical jellium model to understand the electronic properties of small metal particles.[2–7] Whereas in some of the older work the resulting discontinuities in the electronic properties were considered to be artifacts it was—to the best of our knowledge—one of us (W.E.) who came for the first time to the conclusion that "the shell structure of the electronic properties might be a real effect."[2] Afterwards, in his pioneering work, Knight[8] experimentally confirmed this idea and proposed independently the shell structure as *the* order principle in the physical properties of small clusters of the *sp*-bonded metals. In a number of studies[9–11] he was able to show that—whenever a spherical shell shell closing occurs—the experimental values and the theoretically predicted ones agree with each other within 10–20% which is comparable to agreement for the work function predicted by the self-consistent jellium model applied to a metallic half-space[12] and experiment. However, for particle numbers far away from spherical shell closings, the model might be "arbitrarily" wrong and result in rather misleading predictions. It seems to be mainly for this reason that the model was completely misunderstood by some workers in the field.[13–15] In this Brief Report we want to make it clear that the model can be made an excellent one with a high predictive potential if it is only slightly modified to account for shape deformations whenever a shell is open. In this respect the model is the self-consistent analog to Clemenger's application of Nilsson's model of nuclear physics[16] and is in no way arbitrary. It does not contain any parameters to be fitted to experimental data, but relies on the experimental fact[17] that beyond the dimers the bond length is approximately independent of size.

To begin with, let us view some basic features of the self-consistent spherical jellium model. Within the model a metallic cluster to be described is defined by the number of atoms N and the electronic density parameter r_s. Assuming spherical symmetry the cluster radius R is then given by the relation (valid for monovalent metals) $R = r_S N^{1/3}$. The ionic charge is homogeneously smeared out within the sphere of radius R to give a rigid positive background. The electrons move self-consistently in the field of this background and under the influence of their mutual Coulomb interactions.

Very much similar to the restricted self-consistent-field (SCF) calculations for atoms, the spherical symmetry for the effective field is only guaranteed for completely filled shells of a certain type. For incompletely filled shells the spherical symmetry is enforced by spherically averaging the nonspherical electronic charge density of the open-shell structure. If this restriction is lifted, an electrostatic force acting on the jellium background will lead to an aspherical distortion of the latter and, as a consequence, the spherical degeneracy will be lifted, that is to say, the spherical shells will be split into subshells. If we maintain the mean bond distance in going from a sphere to a distorted sphere all the distortions will lead to the same volume. The simplest distortion possible is then that of a spheroid. Within the self-consistent spheroidal jellium model the only additional parameter which comes into play is then the parameter describing the spheroid of equal volume whose semiaxes, in terms of the sphere radius R, are given by

$$Z = \left[\frac{2+\delta}{2-\delta} \right]^{2/3} R \ , \quad X, Y = \left[\frac{2-\delta}{2+\delta} \right]^{1/3} R \ . \tag{1}$$

Obviously, $\delta > 0$ means prolate and $\delta < 0$ means oblate distortion, respectively. Because there is no other principle than the energy-minimization principle, the parameter δ is determined by minimizing the total-energy functional of the system for a given number of particles N and for a given ionic background density r_S. As in our previous work,[2] the Kohn-Sham minimization method of the local-density approximation (LDA) to the density-functional theory (DFT) is used to solve the model. In practice, the Kohn-Sham equations are solved self-consistently for a given distortion parameter δ and the global energy minimum is found as a function of δ.

Due to the cylindric symmetry of the problem, the azimuthal quantum number m is still a good quantum number for the electronic states, as is the parity with respect to reflection at the midplane. However, the angular momentum l is no longer a good quantum number and, as a consequence, the problem is intrinsically two-dimensional. This makes the differential equations a bit harder to solve. This can be done either directly by the relaxation method[18] or—equivalently—by expanding the wave functions into a basis set. We prefer in this work the latter method. Following general ideas of quantum chemistry and taking advantage of the expected behavior of bound-state electronic wave functions in spheroidal coordinates ξ, η, ϕ around the origin[19–21] the following set was adopted:

$$\chi^m_{l,n} = P^m_l(\xi)P^m_l(\eta)e^{-\alpha_n \xi^2}e^{im\phi} \ . \qquad (2)$$

Here, the spheroidal coordinates ξ, η, ϕ are defined as usual,[19] the P^m_l are Legendre functions,[19] and the Gauss exponents α_n are determined in a similar way as in a quantum-chemical calculation.[22] For instance, the bottom s level couples to the above-lying $d,g,\ldots$ levels because of the spheroidal distortions. Because we are already using spheroidal harmonics $P^m_l(\eta)e^{im\phi}$ instead of the spherical harmonics $P^m_L(\theta)e^{im\phi}$, where θ, ϕ are spherical coordinates, only a very few Legendre functions are needed to stabilize the total energy.

Typically, we need three Legendre functions per subshell level and six Gaussian exponents per Legendre function to stabilize the total energy to better than 0.2% with respect to the estimated exact numerical value. However, this instability is not oscillatory, but varies mainly monotonously with increasing particle size, resulting in an estimated instability of 1% in the second difference of the total energy, Δ_2, and 2% in ionization potentials (see below).

Having discussed the method of solution we are ready to present our results. The example we have investigated is a distorted jellium spheroid with an electronic density parameter $r_s = 4$ and numbers of electrons, N, up to 40. Hence, our results are pertaining to small Na clusters.

Traditionally, the first quantity to calculate is the energy per particle. This curve is given in Fig. 1 as a solid line. For comparison, the self-consistent spherical result[2] is reproduced as a dashed line. As can clearly be seen, the spheroidal result has a richer structure because of the various spheroidal subshell closings (this is detailed below). As has been stated in Ref. 8, the energy per particle is not directly related to the abundance spectra of the cluster beam. Instead, the second difference of the total energy, defined as

$$\Delta_2 = [E_{N+1} - (E_N + E_1)] - [E_N - (E_{N-1} - E_1)] \ , \qquad (3)$$

can—under certain conditions—be directly related to sharp edges in the abundance spectra.[23] This quantity is shown in Fig. 2 as a solid line along with the corresponding spherical result. The various subshell closings, which are experimentally visible,[8,9,23] are all clearly resolved. In particular, the strong odd-even effect at small particle numbers can clearly be seen. The microscopic origin of this effect will be discussed below.

The next quantity to be investigated is the ionization potential as a function of size. This quantity, which has been most controversial in the past, is shown in Fig. 3. Surprisingly enough, and of utmost importance the sawtooth behavior of the ionization potential obtained from the self-consistent spherical jellium model is completely destroyed at small N and replaced by a curve which resembles—at least for small particle numbers—the results of the quantum-chemical calculations.[24] Especially interesting is the still large drop of the ionization potential between $N = 8$ and 9, obtained in both approaches. The reason, of course, is that both theories have a shell closing at $N = 8$ and an effective single-electron potential of a high symmetry (because of the weakness of the pseudopotentials).

For Na, relatively old experimental data available in the literature [25,26] are not detailed enough to compare with. However, the recent results by Kappes *et al.*[27] seem to fit our findings.

In particular, the strong odd-even alternation of the ionization potential at small N, as well as its large drop at the main $1p$-shell closing, between $N = 8$ and 9, are nicely reproduced. Interestingly, at larger particle numbers the ionization potential looks like a step curve rather than a sawtooth one. This general trend has been experimentally observed for potassium by Knight *et al.*[18] On the whole, we expect, from the jellium deformation introduced, to improve the agreement between theory and experiment to within the range previously achieved for closed-shell particles.

We now want to discuss the microscopic origin of the various effects we have obtained so far. This can

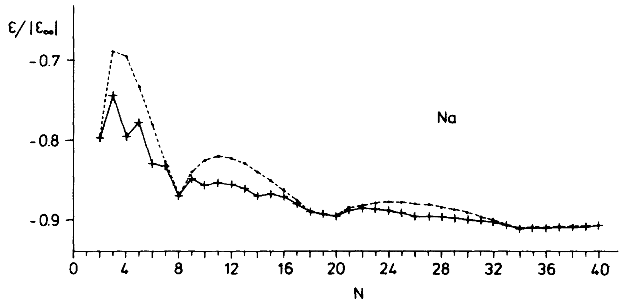

FIG. 1. The energy per particle, in units of the value $|\varepsilon_\infty|$ for the corresponding infinite jellium, for the distorted jellium cluster (solid line) and for the spherical jellium cluster. The results are for Na with $1 < N < 41$.

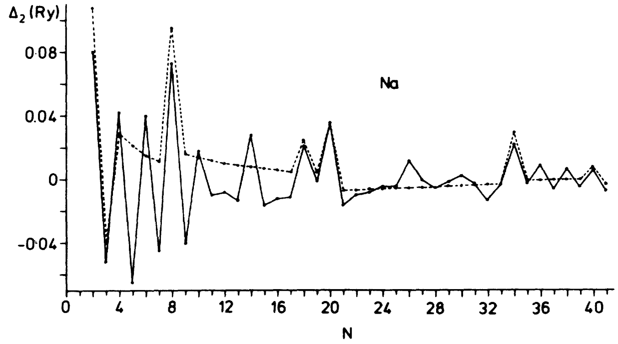

FIG. 2 Second difference Δ_2 of the total energy as a function of N. Solid lines, distorted jellium; dashed line, spherical jellium.

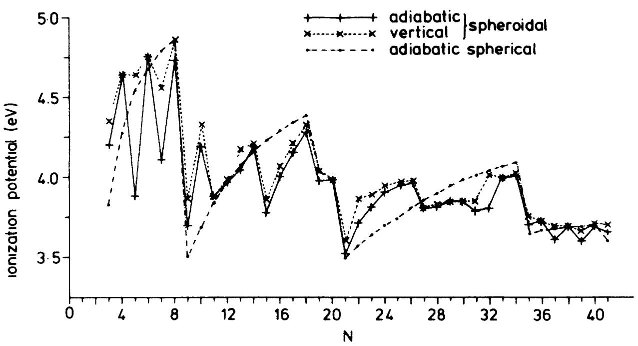

FIG. 3. Ionization potential for a Na particle in various approximations. Note that the spherical sawtooth behavior is completely destroyed after allowing for spheroidal distortions. Originally, it was believed that the strong odd-even alternation at small- particle numbers was a genuine "quantum-chemical" effect. That this is not the case is demonstrated by this figure and is further discussed in the main text.

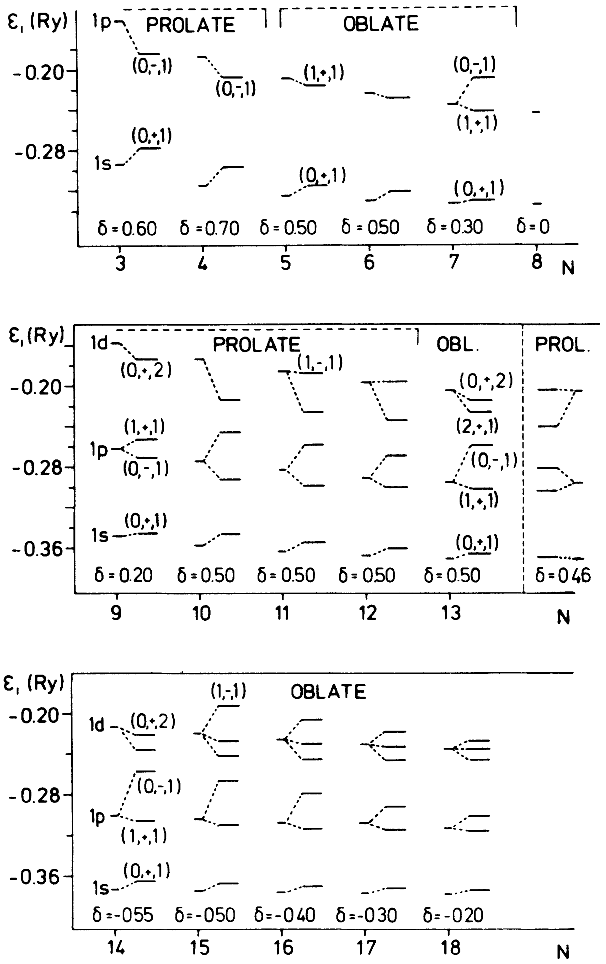

FIG. 4 Evolution of the single-electron level scheme as a function of size, for $3 < N < 18$. For each N, the distortion parameter δ is given. For comparison, the spherical levels are also shown. As can clearly be seen, the spherical shell structure is heavily perturbed for N values in the midshell region. Note that even for $N = 18$ we end up with a spheroidal distortion. For $N = 13$ both oblate and prolate levels are given because the two sets lead to nearly the same total energy of the cluster.

efficiently be done on the basis of the single-particle level scheme obtained from solving the Kohn-Sham equations. In Fig. 4 we show the evolution of the level scheme for particle numbers between 3 and 18, that means in the region of the spherical 1p and 1d shell, respectively. For comparison, the spherical levels are given on the left-hand panel of each particle number. To begin with let us look at $N = 3$: If, in addition to the two electrons residing in the 1s shell, a third electron is accommodated in the (spherical) $1p_z$ level, an electrostatic force acts on the positive background which leads to a cigar-shaped deformation of the latter. Generally speaking, the electrostatic force initializes the distortion, but after that all parts of the total Hamiltonian contribute, leading to the reduction of electrostatic as well as kinetic and exchange-correlation energy. As a consequence, the effective potential widens in the z direction and shrinks in the x,y directions. We end up with a distorted effective potential which has a nearly constant inner value, but is deformed into a dropletlike shape, as in nuclear physics. Hence, our model potential looks like a synthesis of two main ideas of solid-state physics and nuclear physics, without using any new additional parameters. The only assumption which had to be made at the beginning refers to the weakness of the electron-pseudopotential interaction. The validity of this assumption was discussed in detail in our earlier work.[2] Additional support for the dominance of subshell-distortion effects over the pseudopotential contributions was given in the study by Manninen,[29] where the main features of his small ($N \leq 8$) pseudopotential sodium-cluster results agree well with our distorted-jellium picture.

After the "$1p_z$ subshell" is completely filled with two electrons ($N = 4$), the symmetry of the system changes from prolate to oblate at $N = 5$. As a result we have both a reordering and a reoccupation of the single-particle level scheme. The "$1p_{x_1y}$ level" is getting completely filled with four electrons at $N = 6$ and, therefore, for $N = 7$ the now-shifted $1p_z$ level starts filling again. From all the discussion we see that the strong odd-even alternations of the physical properties at small- particle numbers is a direct consequence of the permanent reordering and reoccupation of the level scheme, where the latter effect is, of course, dictated by the Pauli principle. All the discussions could be repeated for the filling of the 1d shell. However, to be brief, we will not do so, but instead conclude by saying that we have found a simple but efficient model for the description of the electronic properties of clusters of the sp-bonded metals. Moreover, it can be successfully extended to investigate their dynamical electronic response properties. Because the model exhibits both the constant potential feature of Sommerfeld's free-electron model of solids and the deformable droplet feature of nuclear physics—without any new parameter—we would like to propose the name "Sommerfeld droplet" to the distorted jellium model applied to small metal particles.

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