Semiclassical analysis of the lowest-order multipole deformations of simple metal clusters

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(October 29, 2018)

We use a perturbative semiclassical trace formula to calculate the three lowest-order multipole (quadrupole $\epsilon_2$, octupole $\epsilon_3$, and hexadecapole $\epsilon_4$) deformations of simple metal clusters with $90 \leq N \leq 550$ atoms in their ground states. The self-consistent mean field of the valence electrons is modeled by an axially deformed cavity and the oscillating part of the total energy is calculated semiclassically using the shortest periodic orbits. The average energy is obtained from a liquid-drop model adjusted to the empirical bulk and surface properties of the sodium metal. We obtain good qualitative agreement with the results of quantum-mechanical calculations using Strutinsky’s shell-correction method.

PACS numbers: 03.65.Sq, 05.30.Fk, 31.15.Ew, 71.10.Ca

Free clusters made of simple metal atoms exhibit a pronounced electronic shell structure [1–3]. Although the detailed experimental information obtained, e.g., from photo-excitation measurements can only be understood if the ionic structure is taken into account [4], the qualitative features of the electronic shell structure can be well described, for not too small systems, by phenomenological deformed shell-model potentials [5,6]. Self-consistent density functional calculations in the framework of a deformed jellium model [5] have revealed that the cluster ground-state shapes can be well characterized in terms of the lowest three multipole orders $\epsilon_2$ (quadrupole), $\epsilon_3$ (octupole), and $\epsilon_4$ (hexadecapole). Since such self-consistent calculations are quite time consuming computationally, it is often more efficient to resort to simpler methods, such as the shell-correction method introduced by Strutinsky in nuclear physics [7], in particular, if more shape degrees of freedom are to be investigated [8].

An even more economical approach is the semiclassical periodic orbit theory (POT) (see, e.g., Ref. [10] for a general introduction), in which quantum oscillations in the level density or other observables can be described in terms of the leading shortest periodic orbits of the corresponding classical system through so-called trace formulæ [11,12]. This method has been used for quadrupole-deformed clusters in a Nilsson-type model [13] and, more recently, using cavities with axial $\epsilon_2$, $\epsilon_3$, and $\epsilon_4$ deformations [14,15]. The approximation of the self-consistent mean field of the valence electrons by a cavity with reflecting walls has received strong support from the quantitative explanation [13] of the experimental magic numbers found in connection with the electronic supershells [14] in terms of the trace formula of the spherical cavity [15]. The validity of the cavity model has also been confirmed by calculations with more realistic Woods-Saxon type potentials [15] and by self-consistent Kohn-Sham calculations [18] in the spherical jellium model.

In Ref. [19], a perturbative trace formula derived by Creagh [19] has been used for axially deformed cavities with small multipole deformations $\epsilon_2$, $\epsilon_3$, or $\epsilon_4$ and found to reproduce the quantum-mechanical results very well for moderate values of the deformation parameters. The main virtue of this approach is that the perturbed orbits need not be known. The trace formula is given in terms of the periodic orbits of the unperturbed system (i.e., here, the spherical cavity), their unperturbed amplitudes being multiplied by a modulation factor that contains the perturbations of their action integrals. The periodic orbits of the spherical cavity were discussed first by Balian and Bloch [12] and characterized by their winding number $t$ (number of revolutions around the centre) and the number $p$ of reflections from the boundary.

In the present work we extend the approach developed in Ref. [17]. The deformed mean field of the electrons is parametrized by an axial cavity whose surface is described in terms of the Legendre polynomials $P_j$ by

$$R(\theta) = R_0 \left( 1 + \epsilon_0 + \sum_{j=2}^{4} \epsilon_j P_j(\cos \theta) \right),$$

where $R = r_0 N^{1/3}$ is the radius of the spherical cavity and $\epsilon_0$ is used to conserve its volume. In contrast to Ref. [17], we include here simultaneously all three deformation parameters $(\epsilon_2, \epsilon_3, \epsilon_4)$ and minimize for each cluster size $N$ the total energy

$$E_{tot}(N, def) = E_{LDM}(N, def) + \delta E(N, def),$$

in order to determine its ground-state deformation. Here $E_{LDM}$ is the average total energy obtained in the liquid drop model (LDM) and $\delta E$ is the shell-correction energy. For the LDM model parameters and the radius constant $r_0$ we use the same values as in Ref. [17]. We evaluate $\delta E$ both quantum-mechanically using the Strutinsky method, and semiclassically by the perturbative trace formula discussed in Ref. [17].

The quantum-mechanical energy spectrum $\{E_i(def)\}$ of the spherical cavities with the shapes defined by [19] was obtained by a method developed in Ref. [20]. In terms of the $E_i(def)$, the exact (quantum-mechanical) shell-correction energy is then defined as usual [8] by
\[ \delta E_{qm} = \sum_{i=1}^{N} E_i - \hat{\lambda} E \bar{g}(E) dE, \]  
whereby \( \bar{g}(E) \) and \( \hat{\lambda} \) are given further below.

We refer to Ref. [13] for the definition of the modulation factor included in the perturbative semiclassical trace formula for the oscillating part \( \delta g_{sc}(E) \) of the level density. When admitting several types of deformations \( \epsilon_j \) simultaneously, the corresponding first-order changes of the classical actions \( \Delta S_j \) have to be added up in the exponent of the integrand for the modulation factor. The semiclassical shell-correction energy \( \delta E_{sc} \) is then obtained using the relation

\[ \delta E_{sc} = \int_0^\lambda E [\bar{g}(E) + \delta g_{sc}(E)] dE - \int_0^{\hat{\lambda}} E \bar{g}(E) dE, \]

where the Fermi energies \( \lambda \) and \( \hat{\lambda} \) are determined iteratively by conserving the particle number:

\[ N = \int_0^\lambda [\bar{g}(E) + \delta g_{sc}(E)] dE = \int_0^{\hat{\lambda}} \bar{g}(E) dE. \]

Here \( \bar{g}(E) \) is the average level density found analytically from its Weyl expansion (see, e.g., Ref. [10]) or by a numerical Strutinsky averaging of the spectrum \( \{E_i\} \).

In Fig. [1] we present deformation energies \( E_{def}(def) = E_{tot}(def) - E_{LDM}(0) \) versus the particle number \( N \) in the region of \( 90 \leq N \leq 200 \). The circles show the quantum-mechanical Strutinsky results for spherical shapes and exhibit three typical shell closures at the magic numbers \( N = 92, 138, \) and \( 186 \). The crosses show the quantum results obtained with deformed shapes, minimizing \( E_{tot} \) for each \( N \) with respect to the three multipole deformations \( \epsilon_2, \epsilon_3, \) and \( \epsilon_4 \). The solid line is the result of the semiclassical calculation including periodic orbits with up to \( t_m = 3 \) repetitions and \( p_m = 30 \) reflections. We see how the inclusion of deformations reduces the total energy drastically, except for the narrow regions around the magic numbers. We obtain a very good agreement of our semiclassical results with the quantum results, showing that the perturbative trace formula works reasonably well even for the largest deformations.

In Fig. [2] we present the three ground-state deformations \( \epsilon_2, \epsilon_3, \) and \( \epsilon_4 \), obtained by the energy minimization procedure, as functions of \( N \). The crosses are the quantum-mechanical results, and the solid and dashed lines are the semiclassical results. The agreement between semiclassics and quantum mechanics is very satisfactory in view of the fact that we cannot expect the semiclassical approximation to be exact. In particular, even the largest deformations agree within about 10% - 20%, in spite of the fact that for these deformations the argument of the modulation factor in the trace formula is larger than unity. A particularly nice result is the correct reproduction of the systematics of octupole deformations \( \epsilon_3 \) which only occur in the lowest part of each shell, as already noticed in Ref. [13]. In addition, the systematic sign change in the hexadecapole deformations \( \epsilon_4 \)
from positive to negative within each shell is reproduced qualitatively, although the negative values turn out to be systematically too small in the semiclassical results. This defect may be connected to the fact that for larger negative hexadecapole deformations the cluster shape becomes a multi-valued function in the cylindrical coordinates. Some minor changes of the deformation systematics are expected when non-axial shapes are used [2], although they can hardly be confirmed experimentally.

The convergence of the semiclassical results with respect to the lengths of the included periodic orbits is demonstrated by the dashed line in Fig. 2 for which \((t_m, p_m) = (1,10)\) was used, whereas the solid line was obtained for \((t_m, p_m) = (3,30)\) as in Fig. 1. We clearly see that a slight improvement is obtained by including the second \((t = 2)\) and third \((t = 3)\) repetitions (harmonics) and the corresponding numbers of reflections.

With the same choice of maximum orbit lengths, we have calculated the deformation energies and ground-state deformations of clusters with up to \(N = 550\) atoms. The results are presented in Figs. 3 and 4. Here the same systematics are found as in Fig. 2 above, although they become less distinct for the larger clusters where the supershells start to decrease in amplitude.

Owing to the efficiency of our method, the numerical calculation of multidimensional deformation energies becomes quite economical. As examples, we show in Figs. 5 and 6 two-dimensional deformation energy surfaces of Na\(_{162}\) and Na\(_{180}\). The deformation energy \(E_{\text{def}}\) is plotted versus quadrupole \((\epsilon_2)\) and hexadecapole \((\epsilon_4)\) deformations. The upper parts give the quantum-mechanical results and the lower parts the semiclassical ones. We see that our semiclassical method captures the correct overall behaviour of the topology of the quantum-mechanical deformation energy landscape, thus being able to reproduce the most prominent isomeric minima correctly.

We have purposely limited our investigations to cluster sizes \(N \gtrsim 90\). Several reasons limit our approach to such particle numbers. First, the selfconsistent total potential (which includes the Coulomb repulsion between the electrons) does not have very steep walls for particle numbers \(N \lesssim 60 - 80\) (cf. [13,17,18]), so that the cavity model cannot be justified. Second, the ionic structure effects become more important for smaller clusters, so that any smooth shell-model potential becomes a bad approximation. Third, the absolute values of the ground-state deformations tend to increase with decreasing particle number (3), so that the perturbative approach will break down for small clusters.

In summary, we have shown that the perturbative semiclassical POT is an efficient and reliable tool for the calculation of ground-state deformations of metal clusters, or of any other system of fermions whose mean field can be approximated by a cavity with reflecting walls. This holds also for atomic nuclei [22], apart from modifications due to the spin-orbit interaction whose inclusion in the POT is still an object of actual research [23,24]. Our method can easily be extended to describe charged clusters by using the relevant liquid drop model developed, e.g., in Ref. [25].

We are grateful to S. Frauendorf for his interest and encouraging discussions at early stages of this work. P.M.
acknowledges the warm hospitality and support of the Bogolyubov Laboratory at Dubna. This work was partially supported by INTAS, the Landau-Heisenberg program, and the Deutsche Forschungsgemeinschaft.

FIG. 5. Deformation energy $E_{\text{def}}$ of Na$_{162}$ versus deformations $\epsilon_2$ and $\epsilon_4$. Upper part: quantum-mechanical, lower part: semiclassical result ($t_m = 3$, $p_m = 30$).

FIG. 6. Same as in Fig. 5 but for Na$_{180}$.

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