

METAL SURFACES AND CLUSTERS: JELLIUM MODEL AND BEYOND IN SEMICLASSICAL VARIATIONAL CALCULATIONS *)

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Abstract: *We report on density variational extended Thomas-Fermi calculations for plane metal surfaces and spherical metal clusters. They reproduce very well, on the average, the earlier microscopic Kohn-Sham results for surface energies and work functions of alkali metals, both using the pure jellium model and including the ionic structure by pseudopotentials, and for finite clusters. For the latter we discuss the average behaviour of total energies, ionisation potentials and electron affinities.*

1. Semiclassical density variational method within the jellium model

The jellium model has been successfully used for the density variational description of metal surfaces [1-4] and spherical metal clusters [5-7], both microscopically using the well-known Kohn-Sham (KS) method [2,3,5] and semiclassically using the extended Thomas-Fermi (ETF) functional [8] of the kinetic energy $T_s[\rho]$ including gradient corrections up to second [6] or fourth order [1,4,7]. In all ETF calculations except that of Tarazona and Chacón [4] who solved numerically the exact Euler variational equation, a restricted variational space of parametrized trial electron densities was used. We propose here to use the following parametrisation for the electron density profile:

$$\rho(z) = \rho_0 \{1 + \exp[(z - Z_0)/a]\}^{-\gamma} \quad (1)$$

in conjunction with the full fourth-order ETF functional [8] for $T_s[\rho]$.

1.a) Metal surfaces

For a plane metal surface ($z =$ normal variable; jellium edge at $z = 0$), $\rho_0 = \rho_{0I}$ is the jellium density, Z_0 is fixed by charge neutrality, so one has two variational parameters a, γ for minimizing the surface tension σ (see refs. [1-4]). To test the quality of (1), our results are compared in Tab. I with recent numerical solutions of the exact Euler variational equation [4] for various Wigner-Seitz radii r_s . We show σ and the work function evaluated by two expressions:

$$W' = [\varphi(\infty) - \varphi(-\infty)] - \mu_b, \quad W = [\varphi(\infty) - \varphi_0] - e_b, \quad (2)$$

$\varphi(z)$ being the electrostatic potential (φ_0 at the jellium edge), μ_b the bulk chemical potential, and e_b the bulk energy per particle. W' is given by Koopman's theorem [2]; W was given by Mahan and Schaich [10] and is identical to W' if exact variational densities are used; for parametrized trial densities W should be used, being less sensitive to details of the density profile [3]. The agreement between our results, which require only little computational effort, and the exact numerical solutions [4] is very good in the whole range of metallic densities, in particular for W . This indicates that (1) is an excellent parametrization of the exact solutions [4], better than the frequently used exponential profile [1].

1.b) Finite spherical clusters

For spherical clusters, we replace in eq.(1) z by the radial variable r and Z_0 by the radius parameter R which is adjusted to fix the number of electrons $\int \rho(r) d^3r = N$. Thus, with ρ_0 , a and γ we have three variational parameters. Minimizing the total energy leads to an excellent reproduction [7] of average results of microscopical KS calculations [5] and of the quantum-mechanical tails of the densities $\rho(r)$. In the following, we present some more systematical calculations using the ETF variational method for spherical metal clusters with Z monovalent atoms. We use the Gunnarsson-Lundqvist LDA functional [9] for exchange and correlation energies.

(i) *Liquid-drop expansion of total energy for neutral clusters:* From our variational ETF results we have determined numerically the surface energy a_s and the curvature energy a_c of the liquid-drop model (LDM) expansion for the total energy of neutral clusters with $Z = N$: $E(Z) = e_b Z + a_s Z^{2/3} + a_c Z^{1/3} + \dots$. In Tab. II we show these coefficients for various r_s , determined by least-square fits to energies of clusters with Z up to 10^5 . The surface energy is related to the surface tension by $a_s = 4\pi r_s^2 \sigma$; it can be seen that this relation is very well fulfilled with the results obtained from the semi-infinite calculations shown in Tab. I, demonstrating the consistency of our approach.

(ii) *Ionisation potential and electron affinity:* In Fig. 1 we present the ETF ionisation potential I and electron affinity A for Na clusters with $8 \leq Z \leq 125'000$ versus $Z^{-1/3}$. Both are shown to approach linearly the correct bulk work function W (not W' !) for $Z^{-1/3} \rightarrow 0$. This holds for all metallic values of r_s , thus representing a numerical improvement over similar older results [6] using less flexible density profiles and truncating $T_s[\rho]$ at second order. The work function $W^*(Z)$ in Fig. 1 is evaluated as W in eq.(2) but in terms

of the variational density profile $\rho(r)$ of the *finite* cluster with Z atoms. Its constancy is remarkable and the fact that the correct bulk work function can be found from the density profile of a cluster with 8 atoms is almost a miracle! - Our ETF results are ideal for determining the slope parameters α , β in the asymptotic expressions $I \simeq W + \alpha e^2/R_I$, $A \simeq W - \beta e^2/R_I$, ($R_I = r_s Z^{1/3}$). These hold even for suprisingly small clusters (see the perfect linear behaviour of I and the almost linear behaviour of A in Fig. 1). Our values of α and β are also given in Tab. II. Unfortunately, the experimental error bars in I , A and W are too large to check our prediction for the r_s dependence of these slopes. We should like to stress that the approximate agreement, found for the lighter alcalines, with the often wrongly [11] assumed 'classical values' $\alpha = 3/8$, $\beta = 5/8$ is *accidental*. In fact, the correct classical value [11] for both these slope parameters is $1/2$. The differences of their values from $1/2$ are due to *quantum-mechanical* effects (kinetic and exchange-correlation energies, tail of electron density). Their contributions can be systematically studied in the LDM expansion of the energy of a cluster with Z atoms and N electrons:

$$E(Z, N) = E_{Coul}^{(0)} + (Z - N)[\varphi(\infty) - \varphi_0] + e_b N + (\text{terms} \propto Z^{2/3} \text{ and } N^{2/3}) + \dots, \quad (3)$$

where the classical Coulomb energy (for squared densities) is

$$E_{Coul}^{(0)}(Z, N) = \frac{3}{5} \frac{e^2}{r_s} \left(\frac{3}{2} N^{5/3} + Z^{5/3} - \frac{5}{2} N Z^{2/3} \right) \quad (N \leq Z) \quad (4)$$

from which the correct asymptotic classical result $I \simeq -A \simeq e^2/2R_I$ is immediately derived. The quantum-mechanical corrections to α and β thus stem from the surface terms in eq.(3); we are presently working on the analytical derivation of these terms.

2. Inclusion of ionic structure by pseudopotentials

It is well known that for high-density metals ($r_s < 3$ a.u.) the jellium model fails in reproducing reasonable surface energies. In the case of finite clusters, the jellium model predicts too low polarizabilities and too high ionization potentials. It is therefore desirable to go beyond this model by taking into account the ionic structure. As in refs. [2,12], we use the local pseudopotentials proposed by Ashcroft [13]. In order to preserve the simplicity of our above variational ETF approach, we use the smooth profiles (1).

2.a) Metal surfaces

We have calculated the face-dependent surface tension σ and work function W for plane metal surfaces. As in [12], the positive charges are smeared out uniformly over each lattice

plane, so that the one-dimensional symmetry is preserved (see this work for the pertinent definitions of σ and W). We compare our results with those of the microscopic non-perturbative KS calculations [12] in Tab. III for different metals and faces. Although some discrepancies are observed for high density metals, the general trends are well reproduced by our semiclassical model, in spite of the simple smooth densities (1). In fact, in the surface region our variational profiles are very similar to the ones shown in [12].

2.b) Spherical metal clusters

The next step is to introduce the pseudopotential model in the semiclassical description of finite clusters. For simplicity and according to calculations by Manninen [14], showing that a relaxed configuration for the ions is more stable than the corresponding ion lattice structure, we preserve spherical symmetry. That is, we smear out the positive charges over a number of spherical shells, whose radii R_1, R_2, \dots and surface charges are variational parameters together with those of the electronic density (1). Doing so, we are able to investigate simultaneously geometric and electronic effects also in a range ($Z \gtrsim 10^3$) where microscopic calculations become prohibitive. So far, we have performed systematical calculations in the medium size range where comparison to microscopic results [15] is still possible. As an example, for Na_{30} , we assume the ions to be distributed on two shells with charges Z_1e, Z_2e . Minimizing the total energy, we obtain $R_1 = 6.6$ a.u., $Z_1 = 10.5$, $R_2 = 10.7$ a.u., $Z_2 = 19.5$, and for the work function $W = 3.95$ eV (to be compared with $W = 3.77$ eV for the jellium model). Since these results are very sensitive to the number of ionic shells, it is crucial to find a criterium to fix it for large clusters in the mesoscopic range. Work along this line, also by microscopic KS calculations, is being pursued.

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Figure 1

Ionisation potential I and electron affinity A for Na clusters (see text for work functions W). Variational ETF results in jellium model.

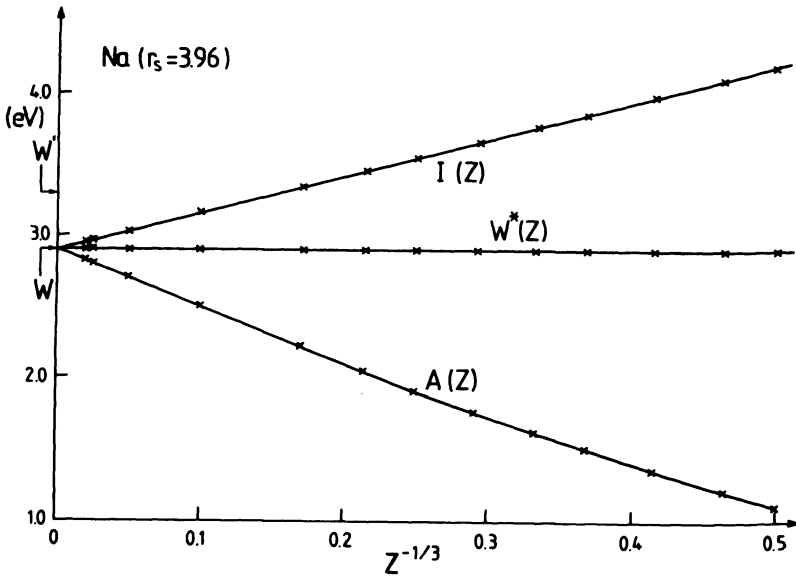


Table I

Surface tension σ (in erg cm^{-2}) and work functions W' , W eq.(2) (in eV) for various Wigner-Seitz radii r_s (in a.u.). Variational ETF results in pure jellium model.

r_s	This work			Ref.[4]	
	σ	W'	W	σ	W
2.0	-1086	3.50	3.54	-1090	3.54
3.0	157	3.44	3.24	153	3.24
4.0	138	3.25	2.91	132	2.89
5.0	87	3.04	2.63	81	2.60
6.0	55	2.82	2.39	50	2.35

Table II

LDM expansion coefficients (definitions see text) of ionisation potentials, electron affinities, and energies of spherical metal clusters. Variational ETF results in pure jellium model. Surface and curvature energies a_s and a_c are in Ry, r_s in a.u.

r_s	α	β	a_s	a_c
2.0	0.426	0.570	-0.06198	0.1282
3.0	0.411	0.587	0.02568	0.0798
4.0	0.401	0.605	0.03642	0.0520
5.0	0.386	0.615	0.03494	0.0376
6.0	0.380	0.620	0.03156	0.0266

Table III

Surface tensions and work functions for various metals. Variational ETF results with plane-averaged pseudopotentials (see text). Results in Ref. [12] are from Table VII.

Units as in Tab.I.

	r_s	[110] if bcc, [111] if fcc				[100] if bcc, [100] if fcc			
		This work		Ref.[12]		This work		Ref.[12]	
		σ	W	σ	W	σ	W	σ	W
K	4.96	114	2.89	135	2.9	146	2.81	147	2.7
Na	3.96	192	3.17	223	3.3	241	3.15	245	3.0
Li	3.28	307	3.76	331	3.5	479	3.44	501	3.4
Pb	2.30	632	5.76	550	3.7	1975	3.78	2155	3.8
Al	2.07	380	3.03	643	4.0	1264	3.77	1460	4.7