

Electronic properties of finite metallic systems

Guy Makov and Abraham Nitzan

School of Chemistry, The Sackler Faculty Of Science, Tel-Aviv University, Tel-Aviv 69978, Israel

(Received 16 June 1992; revised manuscript received 24 August 1992)

The relationship between the surface geometry and certain electronic properties is considered for neutral metal systems. For systems enclosed by surfaces of constant curvature, the total energy, the surface energy, and the chemical potential are found to depend linearly on the surface curvature. Explicit expressions are found for the coefficients of this dependence, in particular for the curvature energy. It is shown that for systems with surfaces of varying curvature a surface charge distribution is formed (and therefore an electric potential varying across the surface), to ensure a constant chemical potential. Implications for the ionization potentials of finite and infinite systems of finite curvature (e.g., spheroids and thin wires) are discussed.

I. INTRODUCTION

The study of finite metallic systems, such as thin films and clusters, has been the object of intensive experimental and theoretical research in the last decade and more.¹ One of the most prominent phenomena to be observed is the size effect on energetic parameters. This manifests itself in an oscillatory behavior about an average asymptotic dependence on system size.¹⁻³ The average trend, by itself, may be studied by continuum models such as the variational scheme of density-functional theory, using approximate expressions for the kinetic, exchange, and correlation energies.⁴⁻⁷ The oscillatory behavior is associated with the detailed electronic structure, and can be obtained, together with the average trend, from Kohn-Sham density-functional calculations. This has been done for spheres and films.^{2,3}

Using the former approach, we and others have studied the averaged size dependence of the ionization (I) and chemical potentials of jellium spheres. Experimentally observed deviations from the predictions of classical electrostatics for small clusters have been traced to quantum-mechanical corrections which give rise to an $O(1/R)$ term in the chemical potential μ of small metal spheres of radius R .⁶ Explicitly, $\mu = -W + C_\mu/R$ (W is the macroscopic work function and C_μ is a constant) and $\mathcal{J} = -\mu + 1/2R = W + C/R$, where $C + C_\mu = \frac{1}{2}$.

It is interesting to consider how this size-dependent behavior depends on the system's geometry. For thin jellium films it has been shown that the chemical potential (work function) is, *on average*, independent of the film thickness, for films of several atomic layers.^{3(a)} This suggests that for such systems the chemical potential (and therefore the ionization potential) is affected by the surface geometry rather than by the linear dimension of the system. We note in passing that calculations based on discrete models have shown dependence of the work function and surface energy on the film thickness.^{1(a),3(a)} Calculations of this sort have been limited to several layers only and seem to converge rapidly to the bulk value.

Deviations may be ascribed to the oscillatory behavior mentioned above and in some cases to the relaxation of the ionic lattice (which is not allowed in jellium).^{3(a)}

In this paper we consider this relationship between the surface geometry and electronic properties of metal systems described by the jellium model. We focus on the average size and shape dependence, ignoring the oscillations associated with the detailed electronic structure as discussed above. In the jellium model different metals are distinguished only by the density of their conducting electrons. The properties we consider are the total electronic energy, the surface energy, and the chemical potential, however, we believe that the treatment proposed below can be extended to other surface electronic properties. We will show that, for systems whose linear size dimensions are greater than a few atomic diameters, these properties are determined only by quantities associated with the corresponding planar surface and by the geometry of the actual surface, which bounds the metal system. The planar surface of the semi-infinite bulk is the limiting case of the present treatment: it is approached when all the linear dimensions go to infinity.

In what follows we first consider systems bound by surfaces with constant curvature (thin films, wires, spherical particles, and spherical vacancies in metals). For such systems we derive a general expression relating the total energy to the volume, the surface area, and the surface energy. We then derive an explicit expression for the surface energy, relating it to the surface curvature, thus obtaining the first explicit expression for the curvature energy of metals. The same framework is used to show that the chemical potential also depends on the surface curvature, thus establishing that systems with different shapes may have different chemical potentials. For systems of nonconstant curvature we show that a surface charge distribution is formed to maintain a constant chemical potential. Finally numerical evaluation of the ground-state energy and the chemical potential is used to test our theoretical predictions. We conclude by discussing our results from the viewpoint of thermodynamics and classical electrostatics applied to "realistic" systems.

II. A GENERAL EXPRESSION FOR THE TOTAL ELECTRONIC ENERGY

Consider a neutral metallic system bound, at least partially, by a surface of constant curvature. This means that all points on the surface are equivalent geometrically and are characterized by the same principal radii of curvature, as in the examples given above. In what follows the coordinates of points near the surface are denoted by (\mathbf{S}, r_\perp) where \mathbf{S} is the position on the surface and r_\perp is the normal distance from it. The surface geometry at a given point \mathbf{S} is characterized by the two principal radii of curvature, or equivalently by the mean, $H(\mathbf{S})$, and Gaussian, $K(\mathbf{S})$, curvatures defined in Eqs. (A2) and (A3), respectively. The metal is defined by the positive background density n_+ , given by

$$n_+(\mathbf{r}) = \begin{cases} n_0 & (r_\perp < 0) \\ 0 & (r_\perp > 0) \end{cases} \quad (1)$$

The ground-state electron density $n(\mathbf{r})$ minimizes the energy functional according to the Hohenberg-Kohn theorem, yielding the ground-state electronic energy.⁴

The energy functional is [in atomic units ($e = \hbar = m_e = a_0 = 1$)] which will be used throughout]

$$E = \int \varepsilon(n; n_+) d^3r \\ = \int \{g(n(\mathbf{r})) + \frac{1}{2}[n_+(\mathbf{r}) - n(\mathbf{r})]\Phi(\mathbf{r})\} d^3r, \quad (2)$$

where $g(n(\mathbf{r}))$ is a function containing the contributions of the exchange, correlation, and kinetic energy terms, and $\Phi(\mathbf{r})$ is the electrostatic potential

$$\Phi(\mathbf{r}) = \int d^3r' \frac{n_+(r') - n(r')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

In what follows we limit ourselves to the local-density approximation.

We now add and subtract the function $g(n_+(\mathbf{r}))$ to the integrand in Eq. (2). Noting that

$$g(n_+(\mathbf{r})) = \begin{cases} g(n_0) = \varepsilon_0 & (r_\perp < 0) \\ g(0) = 0 & (r_\perp > 0) \end{cases} \quad (4)$$

we may write for the total energy

$$E = \varepsilon_0 V + \int d^3r \{g(n(\mathbf{r})) - g(n_+(\mathbf{r})) \\ + \frac{1}{2}[n_+(\mathbf{r}) - n(\mathbf{r})]\Phi(\mathbf{r})\}, \quad (5)$$

where V is the system volume.

To continue, consider the behavior of $n(\mathbf{r})$ far from the surface. Inside the surface it rapidly approaches n_0 while outside it decays to zero. Therefore far from either side of the surface

$$n(\mathbf{r}) \rightarrow n_+(\mathbf{r}).$$

This means that the integrand in Eq. (4) for the energy is nonzero only near the surface. The width Δ of this zone may be estimated from exact Kohn-Sham calculations to be around 5 a.u. (Ref. 5). Therefore the volume integral in Eq. (5) may be transformed into a surface integral of the form (see the Appendix)

$$\int d^3r \rightarrow \int d\mathbf{S} \int_{-\Delta/2}^{\Delta/2} dr_\perp [1 + 2r_\perp H(\mathbf{S}) + r_\perp^2 K(\mathbf{S})] \quad (6)$$

provided

$$\Delta \ll H(\mathbf{S})^{-1}. \quad (7)$$

For surfaces with constant curvature, $H(\mathbf{S})$ and $K(\mathbf{S})$ are independent of \mathbf{S} . Since all surface points are equivalent, $n(\mathbf{r})$ will be independent of \mathbf{S} , i.e., will depend only on r_\perp . Therefore $g(n(\mathbf{r}))$ and $\Phi(\mathbf{r})$ will also be independent of \mathbf{S} . Then the energy functional Eq. (5) may be rewritten as

$$E = \varepsilon_0 V + \sigma A, \quad (8) \\ \sigma \equiv \int_{-\Delta/2}^{\Delta/2} dr_\perp (1 + 2r_\perp H + r_\perp^2 K) \\ \times \{g(n(r_\perp)) - g(n_+(r_\perp)) \\ + \frac{1}{2}[n_+(r_\perp) - n(r_\perp)]\Phi(r_\perp)\}. \quad (9)$$

A is the surface area. Note that even though we use the same notation for $n_+(\mathbf{r})$ and $n_+(r_\perp)$, the former contains all the information about the surface geometry while the latter is a step function which contains no geometrical information. Equations (8) and (9) give the total energy as a sum of volume and surface contributions, where σ may be identified as the surface energy.

III. THE SURFACE ENERGY

Equation (9) defines the surface energy in terms of a one-dimensional integral over a function of the unknown electron density $n(\mathbf{r})$ and the as yet undefined local-density function $g(n)$. Since by definition the integrand is zero outside the range of integration, we may extend the range of integration from $-\infty$ to $+\infty$. We now assume that the unknown electron density $n(\mathbf{r})$ differs only slightly from the electron density of the semi-infinite bulk with a planar surface, $n_p(\mathbf{r})$ [this may be inferred from the results of exact (Kohn-Sham) calculations on jellium spheroids²]

$$\delta n(\mathbf{r}) \equiv n(\mathbf{r}) - n_p(\mathbf{r}), \quad |\delta n(\mathbf{r})| \ll n_p(\mathbf{r}). \quad (10)$$

(The subscript p will denote functions and constants associated with the planar surface.) Therefore to first order in δn Eq. (9) becomes

$$\sigma = \int_{-\infty}^{\infty} dr_\perp (1 + 2r_\perp H + r_\perp^2 K) \\ \times \{g(n_p(r_\perp)) - g(n_+(r_\perp)) \\ + \frac{1}{2}[n_+(r_\perp) - n_p(r_\perp)]\Phi(r_\perp) \\ + [\mu + \frac{1}{2}\Phi(r_\perp)]\delta n(r_\perp)\}. \quad (11)$$

The chemical potential μ is defined by

$$\mu \equiv \frac{\delta E}{\delta n} = \frac{\delta g}{\delta n} - \Phi. \quad (12)$$

Next we wish to expand the expression (11) to first order in H about the planar case, $H = K = 0$. (Note that $H^2 \geq K$ as shown in the Appendix.) The unknown functions $g(n)$, $\Phi(r_\perp)$, and $\delta n(r_\perp)$ may depend on H as may

the chemical potential μ .

Consider first the function $g(n(r_\perp))$. If we make the Thomas-Fermi-Dirac-Gombas-Weizsacker approximation with gradient terms to second order (TFDGW2) and choose the Wigner expression for the correlation energy,⁷ then

$$g(n) = \frac{3}{10}(3\pi^2 n)^{2/3}n + \frac{1|\nabla n|^2}{72n} - \frac{3}{4} \left[\frac{3}{\pi} \right]^{1/3} n^{4/3} - \frac{0.0564 \ln^{4/3}}{0.07953 + n^{1/3}}. \quad (13)$$

$g(n)$ does not depend explicitly on the surface geometry. For this form of g the transformation to surface and surface normal coordinates does not lead to curvature-dependent terms. In what follows we assume that this is true also for the exact $g(n)$.

For $\Phi(r_\perp)$ we assume that the following expansion in the small parameter H is meaningful:

$$\Phi(r_\perp) = \Phi_p(r_\perp) + H\Phi_p^1(r_\perp) + \dots, \quad (14)$$

where $\Phi_p^1(r_\perp)$ is a functional of the electron density of the planar ($H=0$) surface. If the expansion in Eq. (14) is valid then we can expand the spherical case in $1/R$ (which is the mean curvature for a sphere) and find $\Phi_p^1(r_\perp)$.

$$\begin{aligned} \Phi_p^1(x) = & 4\pi \int_{-\infty}^x dx' \{ (x-x')^2 [n_+(x') - n_p(x')] \\ & + n_p^1(x')(x-x') \} \\ & + \int_{-\infty}^{\infty} dx' \{ x'^2 [n_+(x') - n_p(x')] - n_p^1(x')x' \}, \end{aligned} \quad (15)$$

where we also assumed that we may expand

$$\begin{aligned} K_p \equiv & \int_{-\infty}^{\infty} dr_\perp \{ 2r_\perp \{ g(n_p(r_\perp)) - g(n_+(r_\perp)) + \frac{1}{2} [n_+(r_\perp) - n_p(r_\perp)] \Phi_p(r_\perp) \} \\ & + 2\mu_p r_\perp [n_+(r_\perp) - n_p(r_\perp)] + \frac{1}{2} \Phi_p^1(r_\perp) [n_+(r_\perp) - n_p(r_\perp)] + \frac{1}{2} n_p^1(r_\perp) \Phi_p(r_\perp) \}. \end{aligned} \quad (21c)$$

K_p is a constant which depends only on the properties of the planar surface. Here μ_p is the chemical potential of the semi-infinite bulk. The replacement of μ by μ_p is possible if we assume (as will be shown in the next section) that the dependence of μ on the surface geometry is

$$\mu = \mu_p + C_\mu H + O(H^2). \quad (22)$$

The new constant introduced above, K_p , depends only on the properties of the planar surface.

Equation (21a) relates the surface energy of a surface of arbitrary curvature to that of a planar surface of a semi-infinite bulk. Using Eq. (8) we can now obtain the total electronic energy. It should be pointed out that these expressions depend on the particular metal only through the properties of the semi-infinite bulk, while the

$$\delta n \equiv n(r_\perp) - n_p(r_\perp) = n_p^1(r_\perp)H + O(H^2). \quad (16)$$

Next consider the term proportional to μ in Eq. (11),

$$\begin{aligned} & \int_{-\infty}^{\infty} dr_\perp (1 + 2r_\perp H + r_\perp^2 K) \delta n(r_\perp) \\ & = \int_{-\infty}^{\infty} dr_\perp (1 + 2r_\perp H + r_\perp^2 K) [n(r_\perp) - n_p(r_\perp)]. \end{aligned} \quad (17)$$

Charge neutrality determines that

$$\begin{aligned} \int d^3r [n(\mathbf{r}) - n_+(\mathbf{r})] = & A \int_{-\infty}^{\infty} dr_\perp (1 + 2r_\perp H + r_\perp^2 K) \\ & \times [n(r_\perp) - n_+(r_\perp)] = 0, \end{aligned} \quad (18)$$

where A is the surface area. For the special case of the planar surface

$$\int_{-\infty}^{\infty} dr_\perp [n_p(r_\perp) - n_+(r_\perp)] = 0. \quad (19)$$

Applying these results to (17) we obtain

$$\begin{aligned} & \int_{-\infty}^{\infty} dr_\perp (1 + 2r_\perp H + r_\perp^2 K) \delta n(r_\perp) \\ & = 2H \int_{-\infty}^{\infty} dr_\perp r_\perp [n_+(r_\perp) - n_p(r_\perp)] + O(H^2). \end{aligned} \quad (20)$$

Equations (15), (16), and (20) together with our assumption regarding $g(n)$ allow us to rewrite the surface energy in (11) as

$$\sigma = \sigma_p + HK_p + O(H^2), \quad (21a)$$

where

$$\begin{aligned} \sigma_p \equiv & \int_{-\infty}^{\infty} dr_\perp \{ g(n_p(r_\perp)) - g(n_+(r_\perp)) \\ & + \frac{1}{2} [n_+(r_\perp) - n_p(r_\perp)] \Phi_p(r_\perp) \} \end{aligned} \quad (21b)$$

is the surface energy of the semi-infinite bulk,⁸ and where

geometry of a specific surface enters only through its curvature. Thus a thin metal film has the same surface energy as the semi-infinite bulk while a thin wire, which has nonzero curvature, has a different surface energy.

Previous discussions⁹ of the analogous problem for spherical geometry have argued that the energy has the form

$$E = \epsilon_0 V + \sigma A + 2\pi R \gamma, \quad (23)$$

where ϵ_0 is the bulk energy density, σ is the surface energy in a planar geometry, and γ the curvature energy. Equation (21a) implies that γ is related to K_p by

$$\gamma = 2K_p. \quad (24)$$

Previously the curvature energy γ has only been deduced from the fitting of numerical data to Eq. (23). To the best of our knowledge Eqs. (21c) and (24) provide the first explicit expression for γ .

$$\mu = \frac{\delta g}{\delta n} \Big|_n - \Phi = \frac{1}{2} [3\pi^2 n(\mathbf{r})]^{2/3} + \frac{1}{72} \left[\left[\frac{\nabla n}{n} \right]^2 - 2 \frac{\nabla^2 n}{n} \right] - \left[\frac{3}{\pi} \right]^{1/3} [n(\mathbf{r})]^{1/3} - \frac{0.05641 [n(\mathbf{r})]^{1/3} [0.10594 + n(\mathbf{r})]^{1/3}}{\{0.07953 + [n(\mathbf{r})]^{1/3}\}^2} - \int d^3 r' \frac{n_+(\mathbf{r}') - n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (25)$$

We consider a point on the surface of the metal and we transform as before to the local orthogonal curvilinear coordinates (\mathbf{S}, r_\perp) . No dependence on \mathbf{S} is expected and the Laplace operator becomes¹⁰

$$\nabla^2 \rightarrow \frac{d^2}{dr_\perp^2} + 2H \frac{d}{dr_\perp}. \quad (26)$$

The first term is the usual Cartesian term and the second is a contribution arising from the curvature of the surface. Substituting Eq. (26) into Eq. (25) for μ and expanding in the electron density $n(r)$ about its planar value n_p leads to

$$\mu = \frac{\delta g_p}{\delta n} \Big|_{n=n_p} - \frac{4H}{72} \frac{1}{n_p(r_\perp)} \frac{dn_p(r_\perp)}{dr_\perp} + \frac{\delta^2 g_p}{\delta n^2} \Big|_{n=n_p} (n - n_p) - \int d^3 r' \frac{n_+(\mathbf{r}') - n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (27)$$

g_p refers to g , Eq. (14), in which the Laplacian is replaced by its planar form d^2/dr_\perp^2 . The first integral on the right-hand side of (27) is just $\Phi(r)$, which we expand as in (14). Making use of Eq. (16), Eq. (27) becomes

$$\mu = \mu_p - \frac{4H}{72} \frac{1}{n_p(0)} \frac{dn_p(r_\perp)}{dr_\perp} \Big|_{r_\perp=0} - \Phi_p^1(0)H + \frac{\delta^2 g_p}{\delta n^2} \Big|_{n_p} n_p^1(0)H + O(H^2). \quad (28)$$

This result for the chemical potential may be rewritten

$$\mu = \mu_p + C_\mu H + O(H^2), \quad (29a)$$

$$C_\mu \equiv -\frac{4}{72} \frac{n_p^1(0)}{n_p(0)} - \Phi_p^1(0) + \frac{\delta^2 g_p}{\delta n^2} \Big|_{n_p(0)} n_p^1(0). \quad (29b)$$

Equation (29) constitutes a general expression for the chemical potential of any neutral metal system enclosed

IV. THE CHEMICAL POTENTIAL

The chemical potential is defined by the Euler equation (13). Using the TFDGW2 expression, Eq. (14), for $g(n)$ leads to

by a surface of constant curvature. n_p' denotes the derivative with respect to r_\perp . We note that our result for C_μ depends only on the properties of the planar surface, including, however, the unknown function $n_p^1(r_\perp)$. The evaluation of these terms is postponed to Sec. VI.

V. SURFACES WITH NONCONSTANT CURVATURE

So far we have considered only metal systems bound by surfaces of constant curvature. Here we discuss briefly the more general case of nonconstant curvature, using the same arguments as in the constant curvature case. Inserting Eq. (6) in Eq. (2) with no further assumptions yields the general equation for the energy, analogous to Eq. (8),

$$E = \varepsilon_0 V + \langle \sigma \rangle A. \quad (30)$$

The average over the surface of the surface energy $\langle \sigma \rangle$ is defined by

$$\langle \sigma \rangle = \frac{1}{A} \int d\mathbf{S} \sigma(\mathbf{S}), \quad (31a)$$

$$\sigma(\mathbf{S}) \equiv \int_{-\infty}^{\infty} dr_\perp [1 + 2r_\perp H(\mathbf{S}) + r_\perp^2 K(\mathbf{S})] \times \{g(n(r_\perp, \mathbf{S})) - g(n_+(r_\perp)) + \frac{1}{2}[n_+(r_\perp) - n(r_\perp, \mathbf{S})]\Phi(r_\perp, \mathbf{S})\}, \quad (31b)$$

$$\Phi(r_\perp, \mathbf{S}) \equiv \int d^3 r' \frac{n_+(r'_\perp) - n(r'_\perp, \mathbf{S}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (31c)$$

To calculate the surface energy we follow the same arguments of Sec. III, defining

$$\delta n(r_\perp, \mathbf{S}) = n(r_\perp, \mathbf{S}) - n_p(r_\perp) \quad (32)$$

so the surface energy at \mathbf{S} , $\sigma(\mathbf{S})$, may be rewritten, analogous to Eq. (11), as

$$\sigma(\mathbf{S}) = \int dr_\perp [1 + 2r_\perp H(\mathbf{S}) + r_\perp^2 K(\mathbf{S})] \{g(n_p(r_\perp)) - g(n_+(r_\perp)) + \frac{1}{2}[n_+(r_\perp) - n_p(r_\perp)]\Phi(r_\perp, \mathbf{S}) + [\mu + \frac{1}{2}\Phi(r_\perp, \mathbf{S})]\delta n(r_\perp, \mathbf{S}) + O(\delta n^2)\}. \quad (33)$$

$\Phi(r_1, \mathbf{S})$ and μ are defined by Eqs. (31c) and (13), respectively. We assume that the integral in Eq. (31) converges rapidly compared with the variation in the surface geometry, so that only the local geometry need be considered and therefore Φ may be expanded as in Eq. (14) with H replaced by $H(\mathbf{S})$. The term in square brackets in the integrand is identical to that in Eq. (11), with a different form for $\delta n(r_1, \mathbf{S})$. Applying the arguments used to obtain Eq. (20), we get the analogous expression

$$\begin{aligned} & \int d\mathbf{S} \int dr_{\perp} [1 + 2r_1 H(\mathbf{S}) + r_1^2 K(\mathbf{S})] \delta n(r_1, \mathbf{S}) \\ &= \int d\mathbf{S} 2H(\mathbf{S}) \int_{-\infty}^{\infty} dr_{\perp} r_{\perp} [n_+(r_{\perp}) - n_p(r_{\perp})]. \end{aligned} \quad (34)$$

This leads to an averaged form of Eq. (21a),

$$\langle \sigma \rangle = \sigma_p + \langle H \rangle K_p + O(H^2), \quad (35a)$$

where

$$\langle H \rangle = \frac{1}{A} \int d\mathbf{S} H(\mathbf{S}) \quad (35b)$$

and where K_p is defined by Eq. (21c). Equations (30) and (35) give the total electronic energy of a general metal system in terms of the average surface energy. The latter is obtained in terms of the surface average of the local mean curvature. As an example for a prolate spheroid (ellipsoid) of volume V and ratio α between the major and minor axes $\langle H \rangle = 1/R$ for $\alpha = 1$, and $\langle H \rangle = 1.09/R$ and $1.41/R$ for $\alpha = 3.5$ and 10 , respectively, where $R \equiv (3V/4\pi)^{1/3}$.

The chemical potential is constant throughout the system and may be calculated at any point by the Euler equation (12). Unlike Eq. (31) which is an integral expression for the surface energy, the Euler equation is a local equation, the solution of which requires knowledge of the detailed structure of the electron density, $n(\mathbf{r})$. This structure is complex; in particular the existence of non-constant curvature implies the existence of a nonzero surface-charge distribution (a detailed analysis of the case of a jellium hemisphere is given in Ref. 11). This can be seen by considering two metal spheres with radii R_1 and R_2 ($R_1 > R_2$). Equation (29) determines that the electronic chemical potential in sphere 1 is lower than that in sphere 2. At (contact) equilibrium a fraction of an electron charge, δQ , will move (on the average) from sphere 2 (smaller curvature) to sphere 1 (larger curvature) in order to equalize the chemical potential. Furthermore it is obvious that the electric potential on the surface of sphere 1 and sphere 2 will not be the same, i.e., the well-known classical boundary condition of constant electric potential on the surface is not valid for small systems. It follows that for a system of metal colloid particles of different sizes at equilibrium, there are, on average, net (fractional) positive charges on the small particles and net (fractional) negative charges on the larger. Similarly if this system is in equilibrium with a planar surface (electrode) of the same metal, then all the particles will have positive fractional charges.

VI. NUMERICAL RESULTS

In Secs. II–IV we obtained (under some assumptions) general expressions for the total energy and the surface energy of metal systems bound by surfaces of constant curvature, as well as for their chemical potential. These expressions depend on geometry-independent quantities associated with the electronic properties of the corresponding planar surface and on the geometrical properties of the curved surface. In this section we compare our results to numerical solutions for jellium systems.

The general expression for the energy is

$$E = \epsilon_0 V + \sigma_p A + K_p H A. \quad (36)$$

We calculated the energy for spheres and cylinders¹² by the restricted variational method. The details have been described elsewhere.^{6(a),13} The results were fitted to Eq. (36) and ϵ_0 , σ_p , and K_p were extracted. The quality of the fit may be seen in Fig. 1, and the results are shown in Table I. Within our numerical accuracy the parameters ϵ_0 , σ_p , and K_p are the same for the geometries considered.

For the chemical potential we have obtained the expression

$$\mu = \mu_p + C_{\mu} H \quad (37)$$

to which we fitted the numerical results obtained by the methods of Ref. 6(a). μ_p and C_{μ} were extracted and are shown in Table I. The resulting C_{μ} is also seen to be independent of geometry.

For the thin-film geometry, $H = 0$, and we predict the surface energy and the chemical potential will be independent of the film thickness (greater than atomic dimensions) and equal to that of the planar surface of the bulk. Indeed it has been shown that for thicknesses of several atomic layers or more the average chemical potential does not depend on film thickness.^{3(a)} We have confirmed this in our own calculations. Similarly we have found the (average) surface energy to be thickness

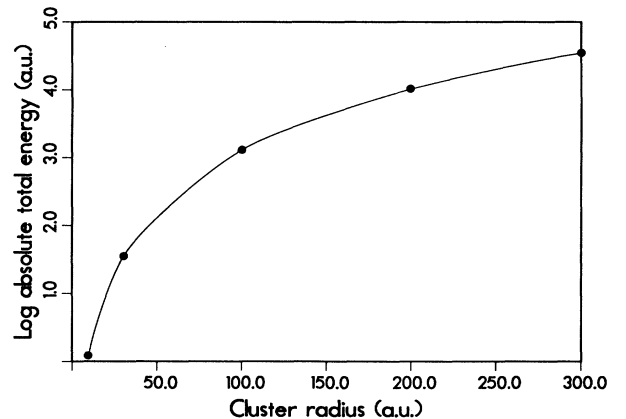


FIG. 1. The base 10 logarithm of the absolute total energy (in a.u.) of jellium spheres ($r_s = 4$) is shown for various sphere radii. The solid line is a plot of the least-squares curve obtained from fitting the data to Eq. (36).

TABLE I. Results for jellium $r_s=4$.

Geometry	ϵ_0	σ_p	K_p	μ_∞	C_μ
Spherical	-0.000 31	-7.1×10^{-5}	0.000 12	-0.097	0.05
Cylindrical	-0.000 31	-6.8×10^{-5}	0.000 12	-0.099	0.05
Planar	-0.000 31	-7.2×10^{-5}	a	-0.097	a
Expressions ^b	-0.000 31	-7.2×10^{-5}	0.000 10	a	0.08

^aNot applicable.

^bEquations (4) and (14) for ϵ_0 , Eq. (20b) for σ_p , Eq. (20c) for K_p , and Eq. (29b) for C_μ .

independent as predicted by Eq. (21a).

Further testing may be done by directly calculating K_p and C_μ . These depend on the unknown functions $n_p^1(r_\perp)$ and $\Phi_p^1(r_\perp)$. The latter may be estimated by expanding in H the functions $n(r_\perp)$ and $\Phi(r_\perp)$ associated with the trial density functions which are solutions of the linear Thomas-Fermi equation.^{7,12,13} The results of these estimates are shown in Table I and they confirm the validity of the assumptions leading to expressions (21) for K_p and (29) for C_μ . The difference between the numerical and theoretical [Eq. (29)] values of C_μ is probably due to the restricted variational procedure we use for the numerical calculation while Eq. (29) for C_μ is based on an unrestricted variation. Indeed the unrestricted variational calculation of Engel and Perdew^{6(b)} yields values of C_μ similar to those obtained from expression (29). This calculation also shows that K_p is strongly dependent on r_s , while C_μ is not. This is confirmed by our present calculation.

VII. DISCUSSION AND CONCLUSIONS

We have shown that the energy, the surface energy, and the chemical potential of metal systems with finite surface curvature H depend on this curvature. We have also obtained an explicit expression for the linear terms of the expansions in powers of H of these quantities. These provide the first-order curvature correction terms to the work function of such systems relative to the underlying planar surface. We have verified these results by numerical calculations.

For systems characterized by nonconstant surface curvature we have obtained a closed expression only for the average surface energy. For such systems we have also shown that the condition of constant chemical potential leads to a redistribution of charge on the surface, with the positive charge concentrated in regions of high curvature and the negative charge in regions of low curvature (note that this implies variation of the electric potential across the surface in contradiction to the classical boundary condition for metal surfaces). In the extreme case of a metal atom adsorbed on a planar surface of the same substance, this implies that the atom will be positively charged. Detailed calculations for lithium⁵ and jellium¹⁶ show that this is indeed the case.

The ionization potential (IP) \mathcal{J} of infinite systems is equal in magnitude to the chemical potential of electrons in these systems. For systems of finite curvature (e.g., a thin wire) Eq. (21) implies that the IP depends on the curvature. Denoting by W the work function associated

with an infinite planar surface ($W = -\mu_p$) we find

$$\mathcal{J} = W - C_\mu H, \quad (38)$$

where for jellium with $r_s=4$, $C_\mu=0.05$. Then for a cylinder of radius R and infinite length (thin wire, $H=1/2R$)

$$\mathcal{J} = W - 0.025/R. \quad (39)$$

We expect the experimental effect to be almost twice as large, as our calculations underestimate C_μ by a factor of 2 compared with the experimental C_μ of metal clusters.

For finite systems removing an electron results in the formation of a positive charge distribution $\delta n(\mathbf{r})$. The IP is given by¹⁴

$$\mathcal{J} = -\mu + E_c, \quad (40)$$

where

$$E_c = \frac{1}{2} \int \int \frac{\delta n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \quad (41)$$

is the electrostatic charging energy, which is zero for an infinite surface and equals (classically) $e^2/2R$ for a sphere of radius R . E_c may be evaluated classically for a prolate spheroid¹⁵ with ratio α between the major and minor axes $E_c=0.43/R$ for $\alpha=3.5$ and $0.32/R$ for $\alpha=10$, where $R=(3V/4\pi)^{1/3}$ (V is the volume). We did not get explicit expressions for the dependence of μ on R and α , but if we assume [in analogy with the surface energy, Eq. (35a)] that $\mu=\mu_p+C_\mu\langle H \rangle$ we can estimate μ from the average curvature, Eq. (35b). For a prolate spheroid we find $\langle H \rangle=1/R$, $1.09/R$, and $1.41/R$ for $\alpha=1$, 3.5 , and 10 , respectively. Using $C_\mu=0.05$ for $r_s=4$ finally yields

$$\mathcal{J} = W + C/R, \quad (42)$$

where $C=0.45$, 0.39 , and 0.25 for $\alpha=1$, 3.5 , and 10 , respectively. Generally C decreases when α increases. The absolute values should be regarded as rough estimates. The value $C=0.45$ for $\alpha=1$ (sphere) is known to be overestimated by $\sim 10\%$; also the relation $\mu=\mu_p+C_\mu\langle H \rangle$ is an unproven approximation.

ACKNOWLEDGMENTS

This work has been supported by the U.S.A.-Israel Binational Science Foundation and by the Israel Academy of Sciences.

APPENDIX: TRANSFORMATION OF INTEGRALS

Consider an integral

$$I = \int d^3r f(\mathbf{r}), \quad (\text{A1})$$

where $f(\mathbf{r})$ is nonzero only in a region of thickness Δ about some surface $\mathbf{S}(\mathbf{r})$. At each point the surface is characterized by the two principal radii of curvature R_1 and R_2 . The mean curvature H and the Gaussian curvature K at a point S on the surface are defined by

$$H = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (\text{A2})$$

and

$$K = \frac{1}{R_1 R_2}. \quad (\text{A3})$$

We note that for all R_1, R_2 ,

$$H^2 \geq K. \quad (\text{A4})$$

If the thickness Δ is much less than the local radius of curvature, i.e.,

$$\Delta \ll H(\mathbf{S})^{-1}, \quad (\text{A5})$$

then the volume to be integrated over may be divided into nonoverlapping tubes, each of which is defined by having its surface normal to $\mathbf{S}(\mathbf{r})$ at their intersection. The cross section of the tube at the surface \mathbf{S} is ΔS . If ΔS is small enough we can define a coordinate r_\perp normal to \mathbf{S} at the center of the tube, such that the volume of the tube is

$$\int_{-\Delta/2}^{\Delta/2} dr_\perp \Delta S(r_\perp). \quad (\text{A6})$$

$\Delta S(r_\perp)$ is the area of the cross section of the tube at a distance r_\perp from the surface. If we denote by x and y the (orthogonal) principal directions at the center of ΔS , then in the limit $\Delta S \rightarrow 0$

$$\Delta S \propto \Delta x \Delta y \quad (\text{A7})$$

and

$$\Delta S(r_\perp) \propto \Delta x(r_\perp) \Delta y(r_\perp). \quad (\text{A8})$$

The constant of proportionality is geometrical in nature and therefore independent of r_\perp . By the definition of the principal radii of curvature we may write

$$\Delta x(r_\perp) = \Delta x \left[1 + \frac{r_\perp}{R_1} \right], \quad (\text{A9a})$$

$$\Delta y(r_\perp) = \Delta y \left[1 + \frac{r_\perp}{R_2} \right], \quad (\text{A9b})$$

so

$$\Delta S(r_\perp) = \Delta S [1 + 2r_\perp H(\mathbf{S}) + r_\perp^2 K(\mathbf{S})], \quad (\text{A10})$$

where we have denoted explicitly the dependence of H and K on their location on the surface. The integral over a single tube is obtained by inserting (A10) in (A6), while the integral over the volume is obtained, in the usual manner of integral calculus, by summing over tubes in the limit $\Delta S \rightarrow 0$ which may be written

$$\int d^3r \rightarrow \int d\mathbf{S} \int dr_\perp [1 + 2r_\perp H(\mathbf{S}) + r_\perp^2 K(\mathbf{S})] \quad (\text{A11})$$

and the integral is

$$I = \int d\mathbf{S} \int dr_\perp [1 + 2r_\perp H(\mathbf{S}) + r_\perp^2 K(\mathbf{S})] f(r_\perp, \mathbf{S}). \quad (\text{A12})$$

¹(a) For a recent overview of the work on clusters see Proceedings of The Fifth International Symposium on Small Particles and Inorganic Clusters [Z. Phys. D **19** (1991); **20** (1991)]; W. R. Halperin, Rev. Mod. Phys. **58**, 533 (1986); M. A. Duncan and D. H. Rouvray, Sci. Am. **251**, 110 (1989); (b) for thin films see I. P. Batra *et al.*, Phys. Rev. B **34**, 8246 (1986), references therein, and Refs. 3 below.

²W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

³(a) F. K. Schulte, Surf. Sci. **55**, 427 (1976); (b) J. C. Boettger and S. B. Trickey, Phys. Rev. B **45**, 1363 (1992), and references therein.

⁴R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

⁵N. D. Lang, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

⁶(a) G. Makov and A. Nitzan, J. Chem. Phys. **95**, 9024 (1991); (b) E. Engel and J. P. Perdew, Phys. Rev. B **43**, 1331 (1991); (c) A. Rubio, L. C. Balbas, and J. A. Alonso, Physica B **167**, 19 (1990).

⁷J. R. Smith, Phys. Rev. **181**, 522 (1969).

⁸N. D. Lang, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1973), Vol. 28, p. 225.

⁹Reference 6(b), and references therein.

¹⁰P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Chap. 1.

¹¹P. C. Das and J. I. Gersten, J. Chem. Phys. **76**, 3177 (1982).

¹²The trial function used for a cylinder of radius R was

$$n(r) = \begin{cases} n_0 + AI_0(kr) & (r < R) \\ BK_0(\lambda r) & (r > R) \end{cases},$$

where I and K are modified Bessel functions.

¹³G. Makov, A. Nitzan, and L. E. Brus, J. Chem. Phys. **88**, 5076 (1988).

¹⁴J. P. Perdew, Phys. Rev. B **37**, 6175 (1988); in *Condensed Matter Theories*, edited by J. Keller (Plenum, New York, 1989), Vol. 4.

¹⁵W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill, New York, 1968), Sec. 5.02.

¹⁶F. Garcias *et al.*, Phys. Rev. B **43**, 9459 (1991).