On the ionization potential of small metal and dielectric particles

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The ionization potential of small metal and dielectric spheres is considered in different frameworks: classical, semiclassical, and quantum mechanical density functional approach. Classical calculations give conflicting results, and the generally accepted result for the ionization potential of a metal sphere of radius R: $W_I(R)$ = bulk work function + $(3/8)q^2/R$ is shown to be wrong, resulting from the classical image potential too close to the metal surface. Using appropriate cutoff to the image potential, the result $W_I(R)$ = bulk work function + $(1/2)q^2/R$ (previously obtained from solvation energy considerations) is recovered. Experimental results on relatively large particles are in agreement with the latter result. For very small clusters, deviations of experimental results from this classical behavior are shown by a density functional calculation to arise from quantum mechanical effects. These are first the spilloff of the electronic wave functions beyond the cluster edge and secondly from exchange and correlation contributions.

I. INTRODUCTION

The ionization potential of small metal particles in vacuum has been the subject of experimental study for more than a decade.[1-3] It has been pointed out[4,5] that classical electrostatics may account for the main features of the observed size behavior though quantum effects are clearly observable for very small clusters. Classical electrostatics (with quantum corrections) have also been used recently by Brus[6] to evaluate the ionization potential of colloidal semiconductor particles. Smith[4] and later Wood[5] have obtained the following simple result for the ionization potential $W(R)$ of a small spherical metal droplet of radius R:

$$W_I(R) = W_{I,\infty} + \frac{3}{8}\frac{q^2}{R}, \tag{1a}$$

where $W_{I,\infty}$ is the work function of the planar metal and q the electron charge. In contrast, Brus' calculation[6] for a dielectric sphere of dielectric constant ϵ yields in the $\epsilon \to \infty$ limit

$$W_I(R) = W_{I,\infty} + \frac{1}{2}\frac{q^2}{R}. \tag{1b}$$

In the present note we attempt to resolve the conflict between these results and to assess the validity of the classical electrostatic calculation. We show that even though Eq. (1a) is a mathematically correct electrostatic limit, the result (1b) is imposed by the requirement that the work associated with a charge crossing the boundary between two dielectric media should approach the difference between the corresponding solvation energies in the limit of large distances.[7] The generalization of Eq. (1b) for a dielectric of finite ϵ is

$$W_I(R) = W_{I,\infty} + \frac{q^2}{2R}\frac{\epsilon - 1}{\epsilon}. \tag{2}$$

For a metal further modification of the classical theory is needed to take into account screening effects.

Equation (1a) has been reported to be in agreement with experimental measurements on sodium[1] and silver[2,5] particles. We find that while the modified electrostatic calculation yields a slightly better agreement with the reported experimental results on the (relatively large) silver particles, the fit to experimental sodium and potassium cluster results is considerably worse. A density functional calculation shows that quantum mechanical effects are very important for small metal particles, in particular for metals of large r_s (low electron density) values. With these effects taken into account we find that agreement with experimental results is restored. We conclude however that the good fit provided by Eq. (1a) was fortuitous.

This paper is constructed as follows: In Sec. II we show how electrostatic theory should be modified in order to satisfy the requirement that the work associated with a charge crossing a boundary separating two media should correspond to the difference between the solvation energies of these media. In Sec. III, we show how this leads to the results (1b) [rather than (1a)] and (2) for the ionization potential of small particles. The effect of finite screening length, expected to be important for very small particles, is discussed in Sec. IV. In Sec. V we present the results of a density functional calculation which show that classical theory is inadequate for very small particles and that the R dependent terms in the ionization potential result from a combination of several contributions both of classical and of quantum mechanical origin. The deviation of experimental observations on small metal clusters from predictions based on Eq. (1b) is shown to arise mainly from quantum mechanical effects.

II. THE MODIFIED ELECTROSTATIC CALCULATION

For completeness we repeat the classical electrostatic calculation[4,5]: The difference between the work needed to remove a point charge q from a point r outside a conducting sphere to infinity and the same work associated with a plane surface is $(r > R)$

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$$\frac{q^2R^3}{2r^2(r^2-R^2)}+\frac{q^2}{R}-\frac{q^2}{4(r-R)}, \tag{3}$$

where R is the sphere radius. In Eq. (3) the first term is the work against the image force on the sphere,[8] the second is the Coulomb work due to the interaction with the opposite charge remaining on the sphere, and the last term is the image work on the plane. For $r=R+h, h\to 0$ the sum of terms (3) goes to the limit

$$\frac{q^2R^3}{2(R+h)(2hR+h^2)}+\frac{q^2}{R}-\frac{q^2}{4h}\xrightarrow{h\to 0}\frac{3}{8}\frac{q^2}{R} \tag{4}$$

which leads to Eq. (1).

While Eq. (4) is the correct mathematical limit of the energy difference obtained from classical electrodynamics, it is known that the $h^{-1}(h\to 0)$ divergence of the image potential is unphysical, and that at distances <1–2 A classical image theory breaks down. This unphysical divergence cancels in the difference taken in Eq. (4), but it is not obvious that it does not leave incorrect finite terms. Also, as shown below, a logarithmic divergence remains in a calculation equivalent to Eq. (4) for a dielectric solid of dielectric constant ϵ rather than a conducting solid.

A quick approximate way to estimate the short distance behavior of the image potential results from considering a planar interface separating two dielectrics with dielectric constants ϵ_1 and ϵ_2 [Fig. 1(a)]. The solvation energy difference between these two dielectrics (the energy needed to transfer a charge q from the bulk of medium 1 to the bulk of medium 2) is, according to the Born theory of solvation,

$$\Delta H=\frac{q_2}{2\delta}\left(\frac{1}{\epsilon^2}-\frac{1}{\epsilon_1}\right), \tag{5}$$

δ, a quantity of dimension length, is interpreted in the Born theory as the radius of the ion under consideration. Consider now the process in which the charge q is carried slowly (adiabatically) first from the bulk of medium 1 to the point Z_1 in medium 1 a distance h from the interface. The work needed to carry out this process is

$$W_1=-\frac{\epsilon_2-\epsilon_1}{\epsilon_1(\epsilon_2+\epsilon_1)}\frac{q^2}{4h}. \tag{6}$$

Similarly, to move the charge q from the point Z_2 to $-\infty$ requires

$$W_2=\frac{\epsilon_2-\epsilon_1}{\epsilon_2(\epsilon_2+\epsilon_1)}\frac{q^2}{4h}. \tag{7}$$

Equations (6) and (7) should correctly give the corresponding work provided that h is not too small. The simplest choice of saturated behavior in the image potential near the surface is to assume that no work is needed in order to move the charge from Z_1 to Z_2. Then the total work needed in order to move q from the bulk medium 1 to that of medium 2 is

$$W_1+W_2=\frac{q^2}{4h}\left(\frac{1}{\epsilon_2}-\frac{1}{\epsilon_1}\right). \tag{8}$$

This work has to be equal to ΔH of Eq. (5) where

$$h=\tfrac{1}{2}\delta. \tag{9}$$

Requirement of consistency between the solvation energy and the interface image potential thus imposes a cutoff on the image potential. In the present work a precise description of the cutoff is not needed and we use the simplest form, constant potential between the points $Z=Z_1=+h$ and $Z=Z_2=-h$ at the interface (Fig. 2).

It should be noted that the emergence of a cutoff in the image potential is directly associated with the finite size δ of the charge and arises from purely classical considerations. A somewhat different route needs to be taken for a conducting phase (i.e., a metal or an ionic conductor). Here in addition the the charge size δ there is another characteristic length—to screening length α. Assuming that for $r>\delta$ the potential associated with the charge q is given by

$$\phi=A\frac{e^{-r/\alpha}}{r};\quad r\geqslant\delta, \tag{10}$$

we can determine A from the requirement that the magnitude of total surrounding charge is equal to the central charge q. This yields

$$\phi=\frac{qe^{-(r-\delta)/\alpha}}{(1+\delta/\alpha)r}. \tag{11}$$

With this potential, the Born theory of solvation leads to the following expression for the solvation energy (relative to vacuum):

$$\Delta H=-\frac{q^2}{2(\delta+\alpha)}. \tag{12}$$

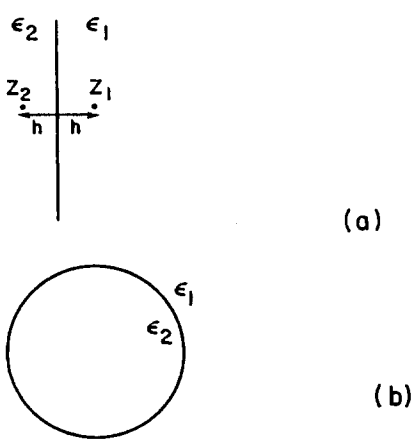

FIG. 1. Configurations discussed in the text.

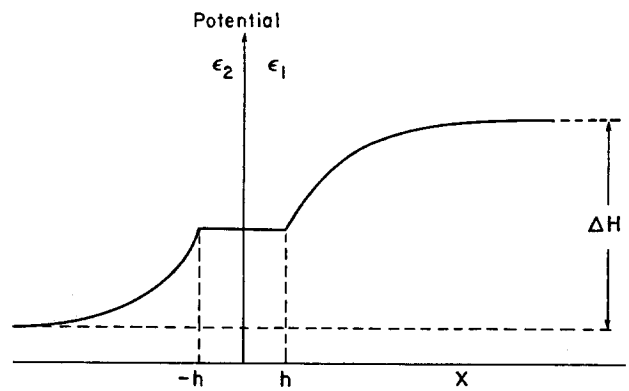

FIG. 2. Potential at the position x of a test charge, near an interface ($x=0$) between two dielectrics. The cutoff at $|x|=h$ is the ansatz made in the paper.

The argument that leads to Eq. (9) above, now yields for an electron at the metal–vacuum interface

$$h = \tfrac{1}{2}(\delta + \alpha) . \tag{13}$$

A plausible choice for δ in this case is k_F^{-1} (k_F is the Fermi wave vector). If we also use for α the Thomas–Fermi result for a free electron gas at $T \ll T_f$, $\alpha = \frac{1}{2}\sqrt{\pi a_0 / k_F}$ (a_0 is the Bohr radius), we get

$$h = \frac{1}{2}\left[k_F^{-1} + \frac{\sqrt{\pi}}{\alpha}\left(\frac{a_0}{k_F}\right)^{1/2}\right] . \tag{14}$$

This result is practically identical to that obtained in semiclassical jellium calculations.[9] To obtain Eq. (14) we have used the simplest screening theory and somewhat arbitrary choice for δ, and indeed later jellium calculations[10] have shown this result to be of only qualitative value. Still the agreement between Eq. (14) and the result of more rigorous calculations serve to show the merit in our present considerations.

For an electrolyte solution Eq. (11) should be replaced by

$$\phi = \frac{q e^{-(r-\delta)/\alpha}}{\epsilon(1+\delta/\alpha) r} , \tag{15}$$

where ϵ is the dielectric constant of the solvent while α is the Debye screening length associated with the ion density. The corresponding solvation energy relative to vacuum is

$$\Delta H = \frac{q^2}{2\delta}\left[\frac{1}{\epsilon(1+\delta/\alpha)} - 1\right] . \tag{16}$$

To end this section it should be noted that even though we have used the term "solvation energy" for ΔH in Eqs. (5), (12), and (16), it may be only part of the measured solvation energy—that which arises from polarization and charge redistribution effects. However, it is the charge redistribution which gives rise to the image force, so the procedure which leads to Eqs. (9) and (13) is valid (or would be if a better theory for screening would be employed). In addition it should be stressed that our simple ansatz concerning the image potential near the interface as displayed in Fig. 2 is too simplistic. The important point is, however, that whatever the correct form is it must obey the requirement of consistency with bulk solvation energies as discussed above.

III. DIELECTRIC SPHERE

We now repeat this calculation for the case of a dielectric sphere [Fig. 1(b)] of radius R. The solvation energy of a charge q in the sphere may be calculated from the following expression for the potential at point $\mathbf{r}$ due to the charge q at point $\mathbf{r}_1$, where both $\mathbf{r}$ and $\mathbf{r}_1$ are in the sphere

$$\phi_2(\mathbf{r}|\mathbf{r}_1) = \frac{q}{\epsilon_2|\mathbf{r}-\mathbf{r}_1|} + \frac{q}{\epsilon_2}\sum_{n=0}^{\infty}\frac{(\epsilon_2-\epsilon_1)(n+1)}{(\epsilon_2+\epsilon_1)n+\epsilon_1} \times \frac{r_1^n r^n}{R^{2n+1}} P_n(\cos\theta); \quad r_1, r < R , \tag{17}$$

where θ is the angle between r and r_1. This leads to an expression,[6(a)] analogous to Eq. (5), for the solvation energy difference for the charge q between point r in the sphere and between the bulk of the surrounding medium 1:

$$\Delta H(r) = \frac{q^2}{2\delta}\left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1}\right) + P(r) , \tag{18}$$

$$P(r) = \frac{q^2}{2\epsilon_2 R}\sum_{n=0}^{\infty}\frac{(\epsilon_2-\epsilon_1)(n+1)}{(\epsilon_2+\epsilon_1)n+\epsilon_1}\left(\frac{r}{R}\right)^{2n} . \tag{19}$$

For the center of the sphere, where $|\Delta H|$ is largest,

$$\Delta H(0) = -\frac{q^2}{2\delta}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1} + \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1} . \tag{20}$$

The second term in Eqs. (18) or (20) which vanishes for $R \to \infty$ represents the loss in solvation energy due to the finite size of the sphere.

This solvation energy difference has to be equal to the work W needed to move the charge q from infinity (i.e., the bulk of medium 1) to the center of the sphere. W may be written as the sum

$$W = W_{\infty,1} + W_{1,2} + W_{2,0} , \tag{21}$$

where $W_{\infty,1}$ is the work to bring q from infinity to the point Z_1 ($r = R + h$), $W_{1,2}$ is the work to take q across the interface from Z_1 to Z_2 ($r = R - h$), and $W_{2,0}$ is the work needed to move q from Z_2 to the center of the sphere. To calculate $W_{\infty,1}$ we use an expression analogous to Eq. (17) for $r, r_1 > R$:

$$\phi_1(\mathbf{r}|\mathbf{r}_1) = \frac{q}{\epsilon_1|\mathbf{r}_1-\mathbf{r}|} + \frac{q}{\epsilon_1}\sum_{n=0}^{\infty}\frac{(\epsilon_1-\epsilon_2)n}{(\epsilon_1+\epsilon_2)n+\epsilon_1} \times \frac{R^{2n+1}}{r_1^{n+1} r^{n+1}} P_n(\cos\theta) . \tag{22}$$

When we use this expression to calculate the work needed to assemble the charge q at point r, the first term contributes to the self-energy of q in medium 1 which is independent of position. The work to bring q from infinity to $r = R + h$ is therefore obtained from the second term of Eq. (22),

$$W_{\infty,1} = -\frac{q^2}{2\epsilon_1(R+h)} \times \sum_{n=0}^{\infty}\frac{n(\epsilon_2-\epsilon_1)}{n(\epsilon_2+\epsilon_1)+\epsilon_1}\left(\frac{R}{R+h}\right)^{2n+1} . \tag{23}$$

For a conducting sphere ($\epsilon_2 \to \infty$) the sum in Eq. (23) is easily evaluated and we get

$$W_{\infty,1} = -\frac{q^2}{2\epsilon_1}\frac{R^3}{(R+h)^2[(R+h)^2 - R^2]} \tag{24}$$

which is the energy associated with the image potential of a charge near a conducting sphere.[7] For finite ϵ_2 we can use the identity

$$\frac{n(\epsilon_2-\epsilon_1)}{n(\epsilon_2+\epsilon_1)+\epsilon_1} = \frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}\left[1 - \frac{\epsilon_1/(\epsilon_2+\epsilon_1)}{n+\epsilon_1/(\epsilon_2+\epsilon_1)}\right] \tag{25}$$

to rewrite Eq. (23) in the form

$$W_{\infty,1} = -\frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}\left[\frac{1}{\epsilon_1}\frac{R^2}{2Rh+h^2} - \frac{1}{\epsilon_2+\epsilon_1}\left(\frac{R}{R+h}\right)^2 \times \sum_{n=0}^{\infty}\frac{[R/(R+h)]^{2n}}{n+(\epsilon_1/\epsilon_2+\epsilon_1)}\right] . \tag{26}$$

The work $W_{2,0}$ may be obtained from Eq. (19),

$$W_{2,0} = P(r=0) - P(r=R-h) = \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1} \times\left[1 - \sum_{n=0}^{\infty} \frac{\epsilon_1(n+1)}{(\epsilon_2+\epsilon_1)n+\epsilon_1}\left(\frac{R-h}{R}\right)^{2n}\right]. \tag{27}$$

Using the identity

$$\frac{\epsilon_1(n+1)}{(\epsilon_2+\epsilon_1)n+\epsilon_1} = \frac{\epsilon_1}{\epsilon_2+\epsilon_1} + \frac{\epsilon_2\epsilon_1}{(\epsilon_2+\epsilon_1)^2}\frac{1}{n+(\epsilon_1/\epsilon_2+\epsilon_1)}, \tag{28}$$

we can rewrite Eq. (27) in the form

$$W_{2,0} = \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1} \times\left[\frac{\epsilon_2+\epsilon_1}{\epsilon_2\epsilon_1} - \frac{R^2}{\epsilon_2(2Rh-h^2)} - \frac{1}{\epsilon_2+\epsilon_1}\sum_{n=0}^{\infty}\frac{1}{n+(\epsilon_1/\epsilon_2+\epsilon_1)}\left(\frac{R-h}{R}\right)^{2n}\right]. \tag{29}$$

From Eqs. (26) and (29) we get

$$W_{\infty,1} + W_{2,0} = \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}\left(\frac{\epsilon_2+\epsilon_1}{\epsilon_1\epsilon_1} - \frac{1}{\epsilon_1}\frac{R^2}{2Rh+h^2} - \frac{1}{\epsilon_2}\frac{R^2}{2Rh-h^2}\right) + S, \tag{30}$$

$$S = \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{(\epsilon_2+\epsilon_1)^2}\lim_{h\to 0} \times\left[\left(\frac{R}{R+h}\right)^2\sum_{n=0}^{\infty}\frac{1}{n+(\epsilon_1/\epsilon_2+\epsilon_1)}\left(\frac{R}{R+h}\right)^{2n} - \sum_{n=0}^{\infty}\frac{1}{n+(\epsilon_1/\epsilon_2+\epsilon_1)}\left(\frac{R-h}{R}\right)^{2n}\right]. \tag{31}$$

Each of the series in Eq. (31) diverges logarithmically for $h\to 0$, however their difference vanishes in this limit (see the Appendix). Neglecting S in Eq. (30) and using

$$\frac{R^2}{2Rh \mp h^2} = \frac{R}{2h} \mp \frac{1}{4} + O(h) \tag{32}$$

yields

$$W_{\infty,1} + W_{2,0} = -\frac{q^2}{4h}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1} + \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1} \times\left(1 + \frac{1}{4}\frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}\right). \tag{33}$$

If, as in the calculation for a planar interface, we assume that for some cutoff distance h, $W_{1,2}$ in Eq. (21) vanishes, we get from $\Delta H(0) = W_{\infty,1} + W_{2,0}$ [using Eqs. (20) and (33)],

$$h = \frac{1}{2}\delta\left(1 + \frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}\frac{\delta}{4R}\right)^{-1} \tag{34}$$

For $R\to\infty$ we recover Eq. (9).

For a metal sphere embedded in the dielectric medium 1, provided that the screening length α is much smaller than R, Eq. (20) is replaced by (in the Thomas–Fermi approximation)

$$\Delta H(0) = -\frac{q^2}{2\delta}\left(\frac{1}{\epsilon_1} - \frac{1}{1+\delta/\alpha}\right) + \frac{q^2}{2\epsilon_1 R}, \tag{35}$$

while Eq. (33) leads to (taking $\epsilon_2\to\infty$)[11]

$$W_{\infty,1} + W_{2,0} = -\frac{q^2}{4\epsilon_1 h} + \frac{5q^2}{8\epsilon_1 R}, \tag{36}$$

where

$$h = \frac{1}{2}\delta\left(1 - \frac{\epsilon_1}{1+\delta/\alpha} + \frac{\delta}{4R}\right)^{-1}. \tag{37}$$

For $\epsilon_1 = 1$ this leads to

$$h = \frac{1}{2}(\alpha+\delta)\left(1 + \frac{\alpha+\delta}{4R}\right)^{-1} \tag{38}$$

which for $R\to\infty$ yields Eq. (13). For finite R the cutoff length h is seen to be R dependent. Again, this particular form for the behavior of the image potential near the interface results from our ansatz. More important is the fact that this behavior should be consistent with the solvation energies in the two media and that the latter should be used to calculate the ionization potential if the exact behavior of the image potential is not known.

The ionization potential of a metal sphere is given by

$$W_I(R) = -(W_{\infty,1} + W_{2,0}) + \frac{q^2}{\epsilon_1 R}, \tag{39}$$

where, to the work $-(W_{\infty,1} + W_{2,0})$ needed to move the electron charge q to infinity, we have added the work $q^2/\epsilon_1 R$ against the Coulomb attraction by the charge $-q$ remaining on the sphere. If we use Eq. (36) to calculate $W_I(R) - W_I(\infty)$ taking h to be R independent we get

$$W_I(R) - W_I(\infty) = \frac{3q^2}{8\epsilon_1 R}$$

which is identical (for $\epsilon_1 = 1$) to Eq. (1). However we have argued that h is R dependent and using this fact, or alternatively using Eq. (35) we get

$$W_I(R) = W_I(\infty) - [\Delta H(0;R) - \Delta H(0;\infty)] + \frac{q^2}{\epsilon_1 R} = W_I(\infty) + \frac{q^2}{2\epsilon_1 R} \tag{40}$$

for the ionization potential of a metal sphere of radius R surrounded by a medium with a dielectric constant ϵ_1.

The ionization potential of a dielectric sphere. In order to obtain the equivalent of Eq. (40) for a dielectric sphere (finite ϵ_2) we have to calculate the solvation energy of a charge q in the sphere of Fig. 1(b), given that a charge $-q$ already occupies a small sphere of radius δ at its center. To this end we use the following expression for the potential at point r in the sphere given that a charge q_0 is at the center and another charge q_1 is at point r_1 ($r, r_1 < R$):

$$\phi_2(\mathbf{r}|\mathbf{r}_1) = \frac{q_0}{\epsilon_2 r} + \frac{q_1}{\epsilon_2|\mathbf{r}-\mathbf{r}_1|} + \frac{q_1}{\epsilon_2 R}\sum_{n=0}^{\infty}\frac{(\epsilon_2-\epsilon_1)}{\epsilon_1(n+1)+\epsilon_2 n} \times \frac{r_1^n r^n}{R^{2n}} P_n(\cos\theta) + \frac{q_0}{R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1}. \quad (41)$$

From Eq. (41), the work required to bring a charge q from the bulk of medium 1 to a distance δ from the center ($\delta \ll R$), given that a charge $-q$ is at the center, is

$$W = -\frac{q^2}{\epsilon_2\delta} + \frac{q^2}{2}\left(\frac{1}{\delta}+\frac{1}{R}\right)\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1}. \quad (42)$$

[Equation (42) is obtained by integrating ϕ_2 with respect to q_1 from 0 to q, replacing q_0 by $-q$, replacing r and $|\mathbf{r}-\mathbf{r}_1|$ by δ and neglecting terms with $(\delta/R)^{2n}$ for $n>0$.] The corresponding ionization potential is $W_I(R) = -W$, so finally

$$W_I(R) = W_I(\infty) + \frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1}. \quad (43)$$

This is a finite ϵ_2 generalization of Eq. (40).

Note that the similar quantity calculated without the opposite charge at the center is the electron affinity of the same dielectric sphere. From Eq. (20),

$$W_{EA}(R) - W_{EA}(\infty) = -[\Delta H(0;R) - \Delta H(0;\infty)] = -\frac{q^2}{2R}\frac{\epsilon_2-\epsilon_1}{\epsilon_2\epsilon_1}. \quad (44)$$

The ionization potential of a dielectric sphere is larger and its electron affinity is smaller from the corresponding bulk quantities by the same amount, $(q^2/2R)(\epsilon_2-\epsilon_1)/(\epsilon_1\epsilon_2)$.

IV. EFFECT OF FINITE SCREENING LENGTH

As stated above, Eq. (35), which leads to Eq. (40), is valid only provided that the particle size is much larger than the screening length. When this is not so we get an additional size dependence term in $W_I(R)$ due to the incomplete screening of the charge q in the metal particle. The resulting correction is sensitive to the screening theory used. Here we limit ourself again to an electrostatic calculation using the Thomas–Fermi theory, keeping in mind that it may be inadequate for these very small sizes.

In the following calculation we consider a classical medium model. The uniform positive charge density is given by $q\rho_+$ where

$$\rho_+ = \begin{cases}\rho_0; & r \leqslant R \\ 0; & r > R\end{cases}. \quad (45)$$

The electrons are assumed to be confined to the spherical volume by an infinite potential barrier at $r=R$. Define

$$f(\mu) = \sum_j \{\exp[\beta(E_j-\mu)]+1\}^{-1}, \quad (46)$$

where E_j is the energy of the jth electronic energy level in this sphere and the sum is over all levels (including spin). ρ_+ is equal to the electron density for the neutral sphere. In this case we denote the electron chemical potential by μ_0. Thus for $r \leqslant R$,

$$\rho_+(r) = \rho_0 = f(\mu_0). \quad (47)$$

When the particle has lost or gained electrons, we may write the electron density as

$$\rho_-(r) = f\{\mu + q[\phi(r) - \bar{\phi}]\}. \quad (48)$$

$\bar{\phi}(r)$ is the spatial average of the local potential $\phi(r)$, so that

$$\int_{r<R} d^3r[\phi(r)-\bar{\phi}] = 0. \quad (49)$$

Note that when $\phi(r) = \bar{\phi}$, the equality $\mu = \mu_0$ holds for any value of $\bar{\phi}$. The electron chemical potential μ for the charged sphere is determined from

$$\int_{r<R} d^3r f\{\mu + q[\phi(r)-\bar{\phi}]\} = \rho_0 V - \eta, \quad (50)$$

where $V = (4\pi/3)R^3$ is the particle volume and where η is the number of electrons lost ($\eta>0$) or gained ($\eta<0$) by the particle. Expanding the integrand in Eq. (50) according to

$$\rho_-(r) = f\{\mu + q[\phi(r)-\bar{\phi}]\} = f(\mu_0) + \left(\frac{\partial f}{\partial\mu}\right)_0[\mu-\mu_0+q(\phi-\bar{\phi})]+\cdots, \quad (51)$$

and using Eqs. (47) and (49) leads to

$$\left(\frac{\partial f}{\partial\mu}\right)_0(\mu-\mu_0) = -\frac{\eta}{V}. \quad (52)$$

In Eqs. (51) and (52) $(\partial f/\partial\mu)_0$ is $[\partial f(\mu)/\partial\mu]_{\mu=\mu_c}$. The local charge density inside the particle is $q\rho$ where

$$\rho = \rho_+ - \rho_- = \frac{\eta}{V} - q\left(\frac{\partial f}{\partial\mu}\right)_0(\phi-\bar{\phi}). \quad (53)$$

The second equality is obtained by using Eq. (51). This leads to the following Poisson equation for the potential ϕ:

$$\nabla^2\phi = -4\pi q\rho = k^2(\phi-\bar{\phi}) - \frac{4\pi q\rho}{V}, \quad (54)$$

where

$$k^2 = 4\pi q^2\left(\frac{\partial f}{\partial\mu}\right)_0 \quad (55)$$

is the square of the Thomas–Fermi inverse screening length. Equation (54) is the starting point of the following electrostatic calculation.

The general solution of Eq. (54) inside the spherical particle is

$$\phi(r) = \bar{\phi} - \frac{\eta q}{r}(Ae^{kr} + Be^{-kr}) + \frac{4\pi\eta q}{Vk^2}; \quad r \leqslant R. \quad (56)$$

The parameters $\bar{\phi}$, A, and B are determined by the conditions

$$\phi(R) = \frac{\eta q}{R}, \quad (57a)$$

$$A + B = 0, \quad (57b)$$

together with Eq. (49). Equation (57a) results from the requirement that outside the sphere $\phi(r) = \eta q/r$, where ηq is the total net charge on the sphere. Equation (57b) insures that $\phi(r)$ is nonsingular for $r=0$. These conditions lead to the following results for the potential:

$$\phi(r) = \eta[\phi_0 + \phi_1(r)], \quad (58a)$$

$$\phi_0 = \frac{q}{R}[1 + A(e^{kR} - e^{-kR})] , \tag{58b}$$

$$\phi_1(r) = -\frac{Aq}{r}(e^{kr} - e^{-kr}) \tag{58c}$$

for its average over the sphere

$$\bar{\phi} = \frac{\eta q}{R} - \frac{4\pi\eta q}{Vk^2} - \frac{A}{R}(e^{kR} - e^{-kR}) , \tag{59}$$

and for the net charge density

$$q\rho(r) = \eta\rho_1(r) , \tag{60a}$$

$$\rho_1(r) = \frac{k^2}{4\pi}\frac{Aq}{r}(e^{kr} - e^{-kr}) . \tag{60b}$$

The work needed to add an infinitesimal charge distribution $\rho_1(r)\delta\eta$ to a spherical particle which already carries a total charge ηq distributed according to Eq. (60) is

$$\delta W = \left\{\int_0^R d^3r[\phi_0 + \phi_1(r)]\rho_1(r)\right\}\eta\delta\eta . \tag{61}$$

The ionization potential, i.e., total work needed to remove an electron from the neutral sphere is therefore

$$\begin{aligned} W_I(R) &= \int_{\eta=0}^{\eta=1}\delta W \\ &= \frac{1}{2}\int_0^R d^3r[\phi_0 + \phi_1(r)]\rho_1(r) \\ &= \frac{1}{2}\phi_0 q + \frac{1}{2}\int_0^R d^3r\,\phi_1(r)\rho_1(r) . \end{aligned} \tag{62}$$

Using Eqs. (58c) and (60b) finally leads to

$$W_I(R) = \frac{q^2}{2R}\left\{1 + \frac{e^{kR} - e^{-kR}}{(kR-1)e^{kR} + (kR+1)e^{-kR}} - \frac{2(kR)^2 + \frac{1}{2}kR(e^{2kR} - e^{-2kR})}{[(kR-1)e^{kR} + (kR+1)e^{-2kR}]^2}\right\} . \tag{63}$$

For $kR \gg 1$ this becomes

$$W_I(R) = \frac{q^2}{2R}\left(1 + \frac{1}{2kR}\right), \tag{64}$$

and for $kR \to \infty$ the limiting result (40) is approached. Note that the result (64) vanishes for $R \to \infty$ so it is just the finite size correction to the bulk work function. The latter originates from a combination of the work against the surface dipole (associated with the electrons spilloff outside the surface) and from quantum mechanical (exchange and correlation energies) contributions; both were omitted from the present calculation. In doing so we have tacitly assumed that the finish size (R) dependence of these terms is absent or weak. The calculation reported next shows that this assumption does not hold in the present situation and that for small particles the size dependence of the ionization potential is affected by these contributions.

V. DENSITY FUNCTIONAL CALCULATION

In this section we repeat the calculation for the work function of a jellium sphere using a simplified density functional framework first explored by Smith[12] for studying the work function associated with planar metal surfaces. The same approach has been recently applied to ground state properties of small metal particles by Das and Gersten,[13] Snider and Sorbello,[14] and Eckart.[15]

In the density functional theory[16] the ground state energy is expressed as a functional of the electron density and a variational procedure is used to obtain the minimum energy configuration. As in Refs. 12–14 we use the functional

$$E = E_{\rm kin} + E_x + E_c + E_{\rm Coul} , \tag{65}$$

where the kinetic ($E_{\rm kin}$), exchange (E_x), correlation (E_c), and Coulomb ($E_{\rm Coul}$) energy functionals are given by

$$E_{\rm kin} = 2.8712\int d^3r\,\rho_-^{5/3}(\mathbf{r}) + \frac{1}{72}\int d^3r\,\frac{|\nabla\rho_-(\mathbf{r})|^2}{\rho_-(\mathbf{r})} , \tag{66}$$

$$E_x = -0.7386\int d^3r\,\rho_-^{4/3}(\mathbf{r}) , \tag{67}$$

$$E_c = -\int d^3r\,\frac{0.056\,41\rho_-^{4/3}(\mathbf{r})}{0.079\,53 + \rho_-^{1/3}(\mathbf{r})} , \tag{68}$$

$$E_{\rm Coul} = \frac{1}{2}q^2\int\int d^3r\,d^3r'\,\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \tag{69a}$$

$$\rho(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r}) . \tag{69b}$$

Equations (66)–(69) are expressed in atomic units so we will set $q = 1$. As in Refs. 12 and 14 (but unlike Ref. 13), we have not included density gradient corrections to the exchange and correlation energies as the magnitude of these corrections is uncertain for the relatively low metallic electron densities of interest.

The calculation reported below is similar to that of Ref. 14, the difference lies in our choice of trial density function. Snider and Sorbello[14] have used the function

$$\rho_-(\mathbf{r}) = \frac{C}{\alpha + \exp[2\beta(r-R)] + \exp[-2\beta(r+R)]} . \tag{70}$$

We use instead a form derived from a potential ϕ which is a generalization of the expressions used in Sec. IV:

$$\begin{aligned} \phi(r) &= \frac{B_1}{r}(e^{kr} + e^{-kr}) + B_0 ; \quad r \leqslant R , \\ &= \frac{C_1}{r}e^{-\lambda r} + \frac{C_0}{r} ; \quad r \geqslant R . \end{aligned} \tag{71}$$

The charge density $q\rho(r)$ is related to $\phi(r)$ through the Poisson equation $\nabla^2\phi = -4\pi q\rho$ using also Eq. (69b) and

$$\rho_+(r) = \rho_0\theta(r - R) \tag{72}$$

[$\theta(x) = 1$ for $x < 0$ and $\theta(x) = 0$ for $x > 0$]. This leads to

$$\rho_-(r) = \begin{cases} \dfrac{k^2}{4\pi q}\dfrac{B_1}{r}(e^{kr} - e^{-kr}) + \rho_0 ; & r < R \\ \dfrac{\lambda^2}{4\pi q}\dfrac{C_1}{r}e^{-\lambda r} ; & r > R \end{cases} . \tag{73}$$

The asymptotic form of $\phi(r)$ ($\sim C_0/r$ for $r \to \infty$) implies that C_0 is the total charge Q on the particle. The other parameters B_0, B_1, and C_1 are determined by the conditions that ϕ and ρ_- (= the absolute square of the electronic wave function) should be continuous at $r = R$ and by the total charge equation

$$Q=\left[(4\pi/3)R^3\rho_0-4\pi\int_0^\infty dr\, r^2\rho_-(r)\right]q\,.$$

These lead to

$$B_0=\left(1+\frac{\lambda^2-k^2}{\mu}\right)\frac{Q}{R}+\frac{4\pi\rho_0 q}{\mu}(1+\lambda R+\eta)\,, \tag{74}$$

$$B_1=-\frac{\lambda^2 Q+4\pi\rho_0 q(\lambda R+1)R}{\mu(e^{kR}-e^{-kR})}\,, \tag{75}$$

$$C_1=\frac{1}{\mu}(-k^2Q+4\pi\rho_0 q\eta R)e^{\lambda R} \tag{76}$$

with

$$\eta=\eta(R)=\frac{(kR-1)e^{kR}+(kR+1)e^{-kR}}{e^{kR}-e^{-kR}}\,, \tag{77}$$

$$\mu=\mu(R)=k^2(\lambda R+1)+\lambda^2\eta(R)\,. \tag{78}$$

The local charge density $q\rho(r)=q[\rho_+(r)-\rho_-(r)]$ is given by

$$q\rho(r)=\begin{cases}-\dfrac{k^2}{4\pi}\dfrac{B_1}{r}(e^{kr}-e^{-kr})\,; & r<R\\[2ex] -\dfrac{\lambda^2}{4\pi}\dfrac{C_1}{r}e^{-\lambda r}\,; & r>R\end{cases}\,. \tag{79}$$

The Coulomb energy is calculated using an expression equivalent to Eq. (69a),

$$E_{\rm Coul}=\frac{1}{2}q\int d^3r\,\phi(r)\rho(r)\,. \tag{80}$$

Using Eqs. (71) and (79) this leads to

$$\begin{aligned}E_{\rm Coul}=&-\tfrac{1}{2}B_0B_1[(kR-1)e^{kR}+(kR+1)e^{-kR}]\\&-\tfrac{1}{4}kB_1^2(e^{2kR}-e^{-2kR}-4kR)\\&-\tfrac{1}{2}\lambda C_1e^{-\lambda R}(\tfrac{1}{2}C_1e^{-\lambda R}+Q)\,.\end{aligned} \tag{81}$$

We note in passing that taking the asymptotic form of Eq. (81) for $kR, \lambda R\gg 1$, then taking $\lambda\to\infty$ leads to

$$E_{\rm Coul}=\frac{Q^2}{2R}\left(1+\frac{1}{2kR}\right), \tag{82}$$

in agreement with Eq. (64). (There the Coulomb energy was taken as the only contribution to the ionization potential.)

With the parameters B_i and C_i given by Eqs. (74)–(76), the trial function (73) is a two parameter (k and λ) function, like Eq. (70), and we expect the two trial functions to give comparable results. We find some small differences as discussed below.

We focus on the $r_s=4$ case because it is relevant to the available experimental results on sodium clusters.[1] In Table I we show some results for this case. We have followed Snider and Sorbello[14] by fitting calculated differences between ion and neutral quantities to the function

$$E_{\rm ion}-E_{\rm neutral}\equiv\Delta E(R)=A+\frac{B}{R}+\frac{C}{R^2}\,. \tag{83}$$

The results for this fit are shown in Table II. There we give values for the parameters A, B, and C for $\Delta E_{\rm kin}+\Delta E_{xc}+\Delta E_{\rm Coul}=\Delta E_{\rm total}=W_I$ as well as for the different contributions $\Delta E_{\rm kin}$, ΔE_{xc}, and $\Delta E_{\rm Coul}$. [Here $E_{xc}=E_x+E_c$ is the sum of the exchange and correlation energies appearing in Eq. (65).] For $\Delta E_{\rm Coul}$ and W_I, the three entries in the table correspond to: (1) a fit based on all cluster sizes between $R=7$ a.u. and $R=100$ a.u.; (2) a fit based on the range $7\leqslant R\leqslant 30$; and (3) a fit for the range $20\leqslant R\leqslant 100$.

TABLE I. Calculated quantities (atomic units, $r_s=4$). E_g is the ground state energy of the neutral cluster and W_I (the ionization potential) is the difference between E_g values of the ionic and neutral species.

	Neutral		Ion			
R	k	λ	k	λ	$-E_g$	W_I[a]
7	1.369	1.329	1.103	1.899	3.925×10^{-1}	1.578(1.561)
10	1.359	1.314	1.261	1.589	1.193	1.391(1.379)
15	1.350	1.298	1.320	1.422	4.147	1.253
20	1.332	1.294	1.319	1.365	9.967	1.185(1.174)
30	1.325	1.283	1.321	1.316	34.08	1.117
40	1.318	1.279	1.316	1.298	81.31	1.082(1.068)
50	1.317	1.275	1.316	1.287	159.4	1.061
70	1.312	1.272	1.312	1.278	439.2	1.037
100	1.313	1.268	1.312	1.271	1284	1.108

[a] In parenthesis are the results of Snider and Sorbello (Ref. 14).

These results lead to the following conclusions:

(a) While the exchange and correlation energies dominate the ionization potential (work function) for the bulk metal (as inferred from the A values in Table II) the R dependence reflects mostly the behavior of the Coulomb energy (it should be kept in mind though that the Coulomb energy is affected by the values of k and λ which are in turn determined also by the other components of the total energy).

TABLE II. Parameters for the fits $\Delta E=A+B/R+C/R^2$. See the text for the meaning of the different entries for $\Delta E_{\rm Coul}$ and W_I.

		$r_s=2$		
		A	B	C
$\Delta E_{\rm kin}$		−0.0634	−0.0471	−0.422
ΔE_{xc}		−0.164	−0.0483	−0.351
$\Delta E_{\rm Coul}$	(1)	−0.0226	0.471	−0.200
	(2)	−0.0228	0.468	−0.188
	(3)	−0.0224	0.489	−0.486
W_I	(1)	−0.123	0.376	−0.271
	(2)	−0.124	0.359	−0.206
	(3)	−0.123	0.408	−0.616
		$r_s=4$		
		A	B	C
$\Delta E_{\rm kin}$		−0.040 2	−0.0773	−0.227
ΔE_{xc}		0.128	0.0239	0.221
$\Delta E_{\rm Coul}$	(1)	0.010 3	0.457	0.111
	(2)	0.011 1	0.436	0.218
	(3)	0.009 89	0.486	−0.246
W_I	(1)	0.098 0	0.403	0.104
	(2)	0.098 6	0.385	0.201
	(3)	0.097 6	0.430	−0.221

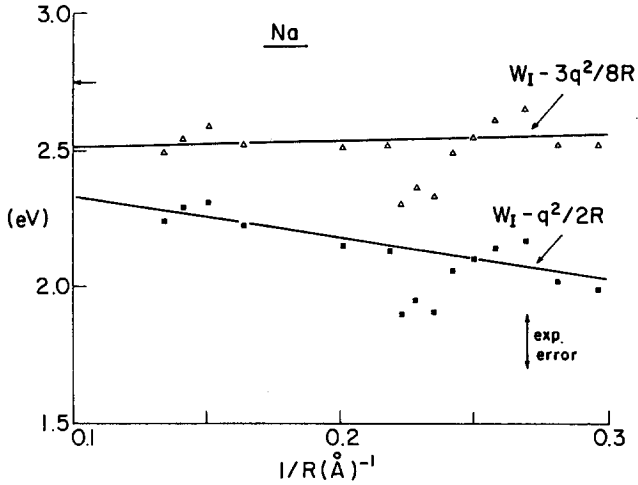

FIG. 3. $W_I(R) - \alpha q^2/R$ for Na. $W_I(R)$ is the observed (Refs. 1 and 19) ionization potential of the sodium cluster of radius R. Triangles: $\alpha = 3/8$, squares $\alpha = 1/2$. The straight lines are obtained from least-square fits of the corresponding results. The arrow at the vertical axis denotes the literature values for the bulk work function.

(b) The kinetic energy provides only a small, practically negligible, part of the total ionization potential of the cluster at all sizes considered.

(c) The value of the parameter B is close to 3/8, the value appearing in Eq. (1a). In particular the value $B = 0.385$ is found to fit best the W_I values of small spheres ($R \leqslant 30$ a.u.) in the $r_s = 4$ case. This may explain the success of Eq. (1a) in fitting the experimental results on Na and K clusters as shown in Figs. 3 and 4. We see however that the apparent success of Eq. (1a) was accidental. The factor 3/8 does not result from electrostatic theory as believed before, but from the compensation of the classical result [Eq. (1b) or (64)] by other corrections. These corrections result from two quantum mechanical effects of different natures: First the spilloff of electron density into the $r > R$ regime as reflected by the finite value of λ. Second, the small but significant contributions of the kinetic and the exchange–correlation terms. Without the latter, the ionization potential would have been given by ΔE_{Coul} which is halfway closer to the classical result than W_I itself. Note that ΔE_{Coul} still contains the quantum spilloff effect [cf. Eq. (81)]. The infinite barrier ($\lambda \to \infty$) limit is given by Eq. (82). [The apparent contradiction between the negative sign of the C coefficients for ΔE_{Coul} in Table II and the corresponding positive term in Eq. (82) results from the fact that in Eq. (82), but not in Table II, the $\lambda \to \infty$ limit was taken.]

(d) For larger clusters, classical contributions are more dominant. This is reflected by the larger values of the B parameter obtained from the fits in the larger sphere regime. This is consistent with the observation (Fig. 5) that Eq. (1b) gives a somewhat better fit than Eq. (1a) to the experimental results on Ag clusters in the R 40–60 a.u. range. (Note however that in these data the particle size distribution have rather large error bars.) For very large clusers $R > 100$, we find that the ionization potential is dominated by the Coulomb term which in turn approaches the limit $Q^2/2R$ for $R \to \infty$.

In Fig. 6, we compile again the experimental results on Na and K clusters, together with the results of the corresponding density functional calculations. The jellium model is not expected to give a very good value of the bulk work function, but as seen from Fig. 6, it accounts well for the trend observed for the cluster size dependence, especially for the Na clusters. For these, the downward shift of the experimental results relative to the theoretical curve reflects the fact that the experimental results of Refs. 1 and 19 do not extrapolate to the accepted value of the Na work function for $R \to \infty$. In fact, fitting these results to the form (83) we find $A = 2.5$ eV. If we subtract this value from the experimental ionization potentials instead of the accepted bulk value (2.75 eV) that was used in Fig. 6, the experimental and theoretical lines for Na would agree within experimental error. For K the discrepancy between the extrapolated ionization potential and the accepted value of the bulk work function is smaller and the corresponding curves in Fig. 6 indeed lie closer to each other. There is however a small unexplained difference in slopes. For Ag (Fig. 7) the fit is again good up to a small vertical shift.

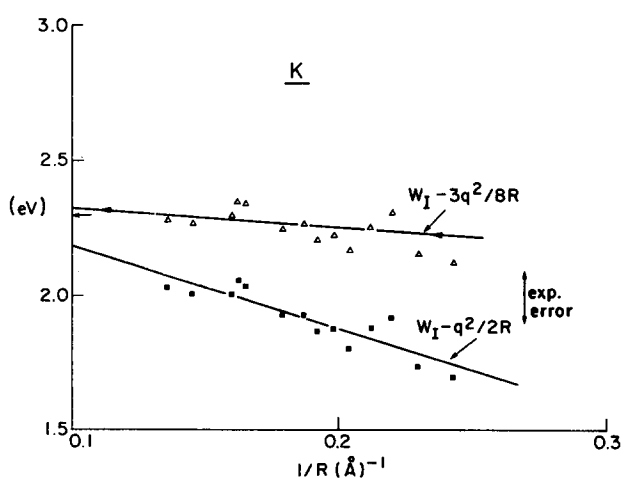

FIG. 4. Same as Fig. 3, for K.

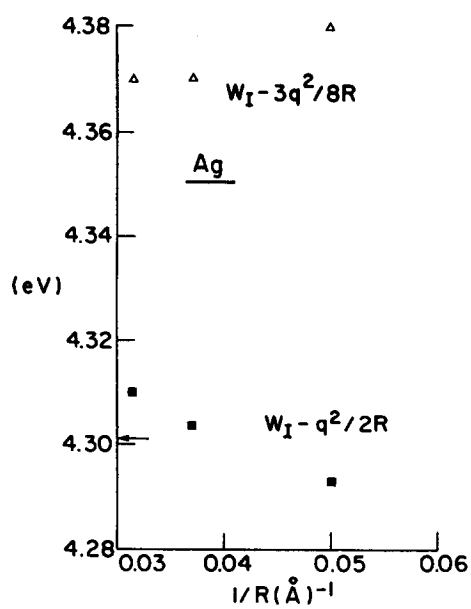

FIG. 5. Same as Fig. 3 (experimental points only), for Ag.

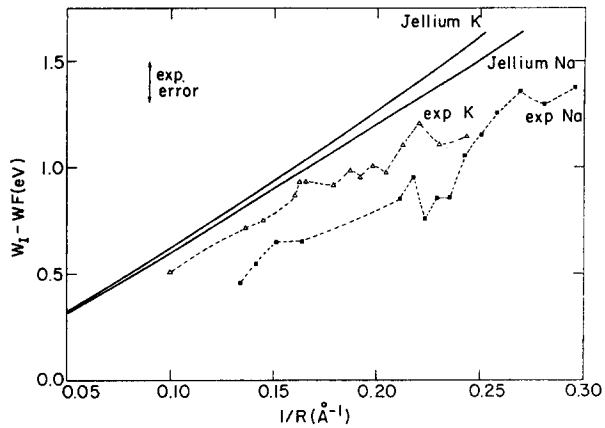

FIG. 6. Experimental results (Refs. 1 and 19) and theoretical jellium calculations for Na and K clusters. The dotted lines connecting the experimental points serve only to lead the eye. The values plotted are the cluster ionization potentials from which the bulk work function was subtracted. For the experimental points this was 2.75 for Na and 2.3 for K. The $R = 10$ Å data point for K is an estimate based on Fig. 2 of Ref. 20. For the jellium results, the values of A (Table II) were used.

We end these discussions with three comments: (a) While calculated ionization potentials successfully account for the experimental observations, the calculated ground state energies are relatively poor, and sometimes become positive [e.g., for $r_s = 2$ and $R = 40$ Å we obtain $E_g = 3.440$. The corresponding result with the Snider–Sorbello trial function, Eq. (70), is 3.397]. This is probably due to the fact that the calculation of the ground state energy based on Eqs. (66)–(69) does not completely eliminate self-interaction of the electrons. This however is expected to make almost no effect on the calculated ionization potentials which involve differences of such ground state energies.

(b) While the crude density functional calculations performed here and in Ref. 14 seem to account well for the general behavior of the cluster size dependence of the ionization potential, they should by no means be taken as conclusive. More elaborate self-consistent density functional calculations[16–18] predict oscillations in W_I as a function of the number of atoms (i.e., of R). Such oscillations are not observed experimentally.[19] The applicability of the density functional approach was recently under some controversy.[19,20]

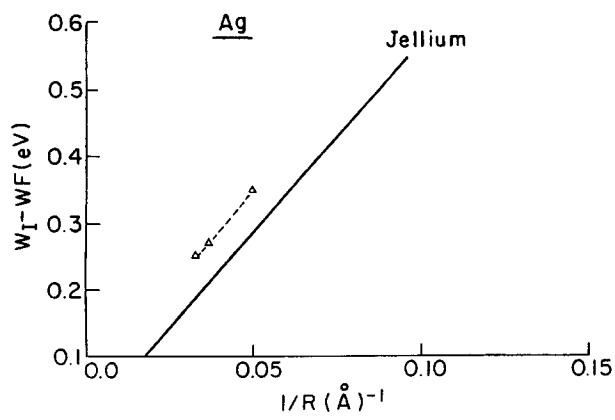

FIG. 7. Same as Fig. 6, for Ag clusters.

VI. CONCLUSION

We have corrected an error in the widely used classical expression [Eq. (1a)] for the ionization potential of small metal spheres. The correct classical result for the size dependent shift of the ionization potential and the electron affinity of a dielectric or a metal sphere is most directly obtained from generalizations of the Born theory of solvation. We have gone in some length into calculating these quantities in a different way, by calculating the work necessary to physically move the charge through the interface. This route leads to results consistent with those based on solvation energies, provided proper cutoffs are used in evaluating the potential near the interface. Erkardt has reached similar conclusions.[21]

The apparent success of Eq. (1a) in accounting for the general trends observed in the ionization potentials of very small metal clusters was shown to result from quantum mechanical corrections to Eq. (1b). For large clusters, Eq. (1b) accounts better for the observations. These observations and the general trends in the experimental results on small Na, K, and Ag clusters are accounted well by a crude density functional calculation.

The size dependent, classical electrostatic ionization potential for a dielectric sphere, leaving a positive charge at the sphere center ($r = 0$), is given by Eq. (43). The analogous r dependent expression has been used as the electrostatic potential in a simple model for the ionization potential of a semiconductor sphere, assuming the ionization leaves a delocalized hole at the top of the valence band.[22] In this case the ionization potential also has a size dependent quantum term, involving an effective mass. Quantitative experimental data for comparison do not appear to be available.

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APPENDIX

Consider the sum

$$\sigma = \sum_{n=0}^{\infty} \frac{x^n}{n+\alpha} = x^{-\alpha} I; \quad \alpha > 0, \tag{A1}$$

$$I = \sum_{n=0}^{\infty} \frac{x^{n+\alpha}}{n+\alpha}. \tag{A2}$$

From Eq. (A2),

$$\frac{dI}{dx} = \frac{x^{\alpha-1}}{1-x}; \quad I(0) = 0, \tag{A3}$$

so

$$I(x) = x^{-\alpha} \int_0^x dy \frac{y^{\alpha-1}}{1-y}. \tag{A4}$$

The term inside the square brackets in Eq. (31) may be written as

$$\left(\frac{R}{R+h}\right)^{2(1-\alpha)} \int_0^{(R/R+h)^2} dy \frac{y^{\alpha-1}}{1-y} - \left(\frac{R-h}{R}\right)^{-2\alpha} \int_0^{(R-h/R)^2} dy \frac{y^{\alpha-1}}{1-y}, \quad \text{(A5)}$$

with $\alpha = \epsilon_1/(\epsilon_2+\epsilon_1)$. The coefficients of each of the integrals in Eq. (A5) are $1+O(h)$. The integrals themselves diverge logarithmically for $h\to 0$, therefore the $O(h)$ terms may be neglected in this limit. We are left with

$$\int_{(R-h/R)^2}^{(R/R+h)^2} dy \frac{y^{\alpha-1}}{1-y} \xrightarrow{h\to 0} \ln\frac{1-(1-h/R)^2}{1-(1+h/R)^{-2}} \to 0. \quad \text{(A6)}$$

[1](a) A. Herrmann, E. Schumacker, and L. Woste, J. Chem. Phys. **68**, 2327 (1978); (b) E. Schumacher, M. Kappes, K. Marti, P. Radi, M. Schar, and B. Schmidhalter, Ber. Bunsenges. Phys. Chem. **88**, 220 (1984).

[2]A. Schmidt-Ott, P. Schurtenberger, and H. C. Siegmann, Phys. Rev. Lett. **45**, 1284 (1980).

[3]For a review and many more references see A. W. Castleman, Jr. and R. G. Keesee, Annu. Rev. Phys. Chem. **37**, 525 (1986).

[4]J. M. Smith, AIAAJ **3**, 648 (1965).

[5]D. M. Wood, Phys. Rev. Lett. **46**, 749 (1981).

[6](a) L. E. Brus, J. Chem. Phys. **79**, 5566 (1983); (b) **80**, 4403 (1984).

[7]Interestingly, Schumacher and co-workers used Eq. (1b) in their earlier paper [Ref. 1(a)], however they later [Ref. 1(b)] replaced it by Eq. (1a), realizing that it is the correct mathematical limit.

[8]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960).

[9](a) D. E. Beck and V. Celli, Phys. Rev. B **2**, 2955 (1970); (b) D. M. Newns, *ibid.* **1**, 3304 (1970).

[10]N. D. Lang and W. Kohn, Phys. Rev. B **7**, 3541 (1973); J. A. Applebaum and D. R. Hamann, *ibid.* **6**, 1122 (1972).

[11]Note that in this case $W_{2,0}=0$ and all the contribution to Eq. (36) arises from W_1.

[12]J. R. Smith, Phys. Rev. **181**, 522 (1969).

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

[14]D. R. Snider and R. S. Sorbello, Solid State Commun. **47**, 845 (1983).

[15](a) P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964); (b) W. Kohn and L. Sham, Phys. Rev. A **140**, 1133 (1965); (c) N. D. Lang, Solid State Phys. **28**, 225 (1973).

[16](a) W. Ekardt, Ber. Bunsenges. Phys. Chem. **88**, 289 (1984); (b) Phys. Rev. B **29**, 1558 (1984); (c) Surf. Sci. **152/153**, 180 (1985).

[17]D. E. Beck, Solid State Commun. **49**, 381 (1984).

[18]M. Y. Chou, A. Cleland, and M. L. Cohen, Solid State Commun. **52**, 645 (1984).

[19]M. M. Kappes, M. Schar, P. Radi, and E. Schumacher, J. Chem. Phys. **84**, 1863 (1986).

[20]W. D. Knight, W. A. DeHeer, W. A. Saunders, K. Clemenger, M. Y. Chou, and M. L. Cohen, Chem. Phys. Lett. **134**, 1 (1987).

[21]W. Ekardt, Ref. 16 and private communication.

[22]Reference 6(a), Sec. B. The final size dependent result, Eq. (9) of this reference, is a positive correction to the bulk ionization potential. However, in the discussion following, the sign convention for ionization potential is used incorrectly. Thus, the result, Eq. (9), is an increase and not a decrease in the bulk ionization potential. In the case of electron capture yielding a negatively charged sphere with an electron delocalized at the conduction band bottom, Eq. (9) is a decrease in the electron affinity, as stated in the discussion.