

# On the nonclassical asymptotic behavior of electronic properties in metal clusters

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The ionization potential  $I(R)$  of small metal spheres (of radius  $R$ ) as well as the electronic chemical potential  $\mu(R)$  in such particles are considered within a three-parameter variational local-density-functional calculation. The asymptotic ( $R \rightarrow \infty$ ) deviations of  $I(R)$  and  $\mu(R)$  from their bulk values behave as  $C/R$  and  $C_\mu/R$ , respectively, where within the computational accuracy  $C + C_\mu = 0.5$ . These results are quantitatively similar to those obtained from a recent variational calculation by Engel and Perdew (EP), and identify the origin of the deviation of  $C$  from its classical value of 0.5 in the size dependence of  $\mu(R)$ . While EP show that this size dependence originates from the gradient terms in the energy functional, we find that its magnitude results from a delicate balance between different contributions. The classical limit  $C = 0.5$  is approached when both  $Z$  and  $R$  are large, where  $Z$  is the number of electrons involved in the transition. These results also lead to the resolution of an apparent paradox recently described by van Staveren *et al.*

## I. INTRODUCTION

The size-dependent ionization potential of small metal clusters has been the focus of intensive research for more than a decade.<sup>1</sup> The average size dependence is found to obey asymptotically ( $R \rightarrow \infty$ ),

$$I(R) = WF + C/R. \quad (1)$$

$WF$  is the bulk work function and  $C$  is a constant. Experiments on simple metals<sup>2</sup> have found  $C$  in the range 0.33–0.40 (in atomic units). The theoretical interpretation of this result has been a matter of some controversy.<sup>2–4</sup> A simple calculation based on classical image theory leads<sup>4</sup> to  $C = 3e^2/8$ , where  $e$  is the elementary charge, in excellent agreement with experimental results. Several authors<sup>3</sup> have pointed out that the correct classical result is  $C = e^2/2$ , and that the observed deviation of the experimental results from this value has a quantum-mechanical origin. Perdew<sup>3(b)</sup> suggested that  $C = C(R) \rightarrow 1/2$  as  $R \rightarrow \infty$ , and a similar trend appears to exist in the calculation of Makov, Nitzan, and Brus,<sup>3(a)</sup> who, however, did not carry out calculations beyond  $R = 100$  a.u. Recent calculations by Seidl, Spina, and Brack,<sup>5</sup> using a restricted variation of a local-density approximation energy functional for jellium spheres, have indicated that  $C \rightarrow 0.40 \pm 0.02$  as  $R \rightarrow \infty$ . Engel and Perdew<sup>6</sup> (EP) have very recently performed an unrestricted variation of this functional by solving directly the Euler equation in order to calculate the asymptotic size dependence of the chemical potential,  $\mu$ ,

$$\mu(R) = \mu(\infty) + C_\mu/R. \quad (2)$$

They propose that the size dependence of the ionization potential is related to that of the chemical potential by

$$I(R) = -\mu(R) + \frac{1}{2} \frac{e^2}{R}. \quad (3)$$

Their calculation leads to  $C_\mu \approx 0.08$ . Furthermore, they

have identified the origin of this size dependence to be in the gradient terms of the kinetic-energy functional [ $T_2$ , Eq. (5f) below, as well as terms of higher order in  $\nabla n$ , where  $n$  is the electron density].

We note in passing that the difference between  $I(R) = E[n-1] - E[n]$  and  $\mu(R) = \delta E[n]/\delta n$  is in a sense a quantum effect, resulting from the discreteness of the electron charge. These quantities are of course equal to each other in the limit  $R \rightarrow \infty$ .

The EP calculation assumes that the origin of the deviation of  $C$ , Eq. (1), from the classical value of 1/2 is in the size dependence of the chemical potential, and it traces the quantum origin of this effect. It is of interest to check whether similar results are obtained from the much simpler variational approach of our earlier work, using a three-parameter variational expression for the electron density. In the present note we calculate the chemical potential within our restricted variational scheme and show that it leads to results similar to those of EP. We also confirm the validity of Eq. (3) by calculating independently both the ionization potential and the chemical potential. In contrast to EP we show that the magnitude of the effect is not always determined by the electronic kinetic energy. Finally, we discuss the classical limit of the cluster ionization process. In particular, we show that the classical charging energy  $W = (Ze)^2/2R$ , where  $Z$  is the number of electrons transferred, is obtained only in the limit of large  $Z$ , where the charging process is essentially continuous.

## II. VARIATIONAL DENSITY-FUNCTIONAL CALCULATION

The model considered is a jellium sphere of radius  $R$  with the positive background given by

$$n_+(r) = n_0 \theta(r-R) = \frac{3}{4\pi r^3} \theta(r-R). \quad (4)$$

$r_s$  is the radius of the Fermi sphere. The ground-state electronic energy  $E$  is a functional of the electronic density  $n(r)$ . For this functional we take the Thomas–Fermi–Dirac–Gombas Weizsacker expression including second-order gradient terms in the kinetic energy and the Wigner expression for the correlation energy.<sup>7</sup> This functional,  $E[n]$ , is the sum of the kinetic ( $T = T_0 + T_2$ ;  $T_4$  and higher-order gradient terms are neglected), exchange ( $E_x$ ), correlation ( $E_c$ ), and Coulombic ( $U$ ) terms:

$$E = T_0 + T_2 + E_x + E_c + U, \quad (5a)$$

where (in atomic units)

$$E_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int [n(r)]^{4/3} d^3r, \quad (5b)$$

$$E_c = -\int \frac{0.056 [n(r)]^{4/3}}{0.079 + [n(r)]^{1/3}} d^3r, \quad (5c)$$

$$U = -\frac{1}{2} \int n(r) \phi(r) d^3r,$$

$$\phi(r) = \int d^3r' \frac{n(r') - n_+(r')}{|r - r'|}, \quad (5d)$$

$$T_0 = \frac{3}{10} \int d^3r [3\pi^2 n(r)]^{2/3} n(r), \quad (5e)$$

$$T_2 = \frac{1}{72} \int d^3r \frac{|\nabla n(r)|^2}{n(r)}. \quad (5f)$$

The variational problem at hand is the minimization of  $E[n]$  subject to the constraint

$$Q = \int d^3r [n(r) - n_+(r)], \quad (6)$$

where  $Q$  is the net charge on the sphere. This leads to the functional

$$J[n] = E[n] - \mu \int d^3r n(r) \quad (7)$$

whose minimization yields  $n(r)$  and  $\mu$ . When this is done by unrestricted variation, the resulting  $\mu$  is the chemical potential, since  $\delta J / \delta n = 0$  leads to  $\mu = \delta E / \delta n$ . In this case  $\mu$  can also be written as

$$\mu = \int d^3r f(r) \frac{\delta E}{\delta n} \bigg/ \int d^3r f(r) \quad (8)$$

with any function  $f(r)$ . The choice of  $f(r)$  makes no difference to the value of  $\mu$  itself; however, it affects the results for the different components of  $\mu$  [associated with the different components of  $E[n]$ , Eq. (5a)]. Engel and Perdew<sup>6</sup> have calculated  $\mu$  and its components from Eq. (8), using

$$f(r) = -\frac{1}{n_0} \frac{\partial n(r)}{\partial r}. \quad (9)$$

This choice of  $f(r)$  is arbitrary and seems to lack physical motivation. A physically more appealing choice is

$$f(r) = n(r; Q=0) - n(r; Q=1). \quad (10)$$

For the choice (10), the incremental electron density used for calculating the first variation of the different components of  $E$  is taken to be proportional to the actual change in  $n(r)$  associated with the removal of one electron from the cluster.

In our present calculation  $n$  is restricted to be of a particular form  $n(r, \{\beta\})$  determined by the set of  $N$  parameters  $\{\beta_i\} = \beta_1, \beta_2, \dots, \beta_N$ . For this restricted form of  $n$ ,  $J[n]$  becomes a function  $J(\{\beta\})$  of the variational parameters and the variational equations are

$$\frac{\partial J(\{\beta\})}{\partial \beta_i} = 0, \quad i = 1, 2, \dots, N. \quad (11)$$

These  $N$  equations together with Eq. (6) determine the  $N + 1$  unknowns  $\{\beta\}$  and  $\mu$  for a given net charge  $Q$ . The ionization potential is determined from

$$I = E(Q=1) - E(Q=0), \quad (12)$$

and the electron affinity is

$$A = E(Q=-1) - E(Q=0). \quad (13)$$

This then yields the size dependence of  $I$  and  $A$  as well as the chemical potential  $\mu$  within this restricted variational approximation. The calculation of  $I$  is similar to that of Ref. 3(a) (except that we now extend the calculation to larger cluster radii). The new element in the present calculation is the evaluation, within the same model, of the chemical potential and its size dependence. Denoting

$$E[n] \equiv E(\{\beta\}), \quad \int d^3r n(r) \equiv S(\{\beta\}), \quad (14)$$

Eq. (11) leads to

$$\mu = \frac{\partial E(\{\beta\})}{\partial \beta_i} \bigg/ \frac{\partial S(\{\beta\})}{\partial \beta_i} \quad (15)$$

for any  $\beta_i$ ,  $i = 1, \dots, N$ . Note that Eq. (15) can be replaced by the linear combination

$$\mu = \sum_i \Delta \beta_i \frac{\partial E(\{\beta\})}{\partial \beta_i} \bigg/ \sum_i \Delta \beta_i \frac{\partial S(\{\beta\})}{\partial \beta_i} \quad (16)$$

for any set of weight coefficients  $\Delta \beta_i$ . In analogy with Eq. (10) the most appealing choice for the parameters  $\Delta \beta_i$  is  $\Delta \beta_i = \beta_i(Q=0) - \beta_i(Q=1)$ .

As in our previous work,<sup>3(a)</sup> we consider a restricted variation over the trial family of densities

$$n(r) = \begin{cases} (A/r)(e^{kr} - e^{-kr}) + n_0 & (r < R), \\ (B/r)e^{-\lambda r} & (r > R). \end{cases} \quad (17)$$

The parameters  $A$ ,  $B$ ,  $\lambda$ , and  $k$  are related by the continuity condition

$$B = Ae^{\lambda R}(e^{kR} - e^{-kR}) + Rn_0 e^{\lambda R}. \quad (18)$$

This leaves us with three independent parameters to be determined by the variation under the constraint (6). Note that this trial density is the exact solution for the linearized Thomas–Fermi formulation of this problem, and that under the further restriction,  $k = \lambda$ , it is the spherical generalization of the trial density used by Smith<sup>7</sup> in calculating the work function of a planar jellium surface.<sup>8</sup>

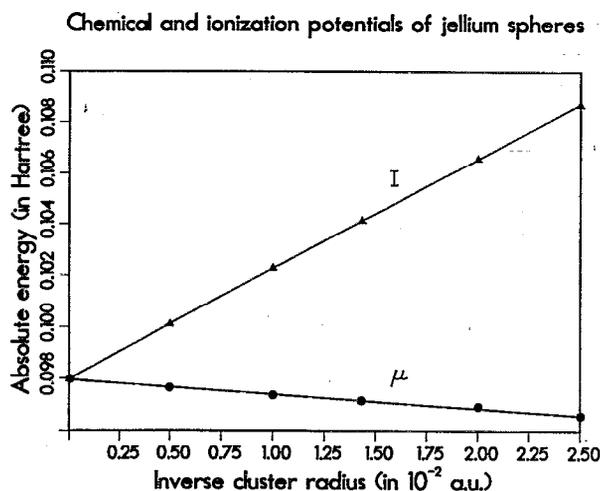


FIG. 1. The absolute magnitudes of the chemical and ionization potentials of jellium spheres with  $r_s = 4$  plotted against the inverse cluster radius. The points are the results of the present variational calculation.

### III. RESULTS

Using the procedure described in Sec. II, we have calculated the ionization and the chemical potentials of jellium spheres with radii in the range 30–200 a.u. An example for  $r_s = 4$  is shown in Fig. 1. The results are represented very well by a straight line vs the inverse radius [as in Eq. (1)].

We found the bulk work function and the bulk chemical potential from the intercepts, and their size-dependence parameters  $C$  and  $C_\mu$  from the slopes. The results are summarized in Table I. The numerical uncertainty in the computed value of the chemical potential is ca. 1%–2%. This estimate was obtained by comparing the calculations of  $\mu$  by Eq. (16) with those obtained from Eq. (15). As expected, the magnitudes of the bulk work function and of the chemical potential are equal within our numerical accuracy. In Table I we show also the results for  $\mu$  and  $C_\mu$  obtained from the unrestricted variational calculation of EP,<sup>6</sup> and the results for  $WF$  and  $C$  from the variational calculation of Seidl, Spina, and Brack.<sup>5</sup> Our results compare well with those of Engel and Perdew,<sup>6</sup> even though these authors included in the energy functional the  $T_4$  term of the kinetic-energy gradient expansion.

For the size-dependence parameter of the ionization potential,  $C$ , we find  $C = 0.42$ – $0.44$  and a decreasing trend in  $C$

as  $r_s$  increases. The size-dependence parameter of the chemical potential,  $C_\mu$ , is found to be in the range 0.05–0.08 compared to approximately 0.08 found by EP.<sup>6</sup> The sum of  $C$  and  $C_\mu$  is  $0.5 \pm 0.02$  for all values of  $r_s$  examined. This is in agreement with the proposition, Eq. (3), relating the non-classical size dependence of the ionization potential and of the chemical potential.

Next, consider the contributions of the various terms in the energy functional to the chemical and ionization potentials, as described in Sec. II. The results of such a calculation for  $r_s = 4$  are presented in Table II. These results were obtained as before by fitting these individual contributions to straight lines vs the inverse cluster radius. The striking similarity between the contributions of the individual energy terms to the chemical and ionization potentials clearly indicates the validity of the Eq. (3) relating the two quantities. Note, however, the difference in the Coulombic energy contribution: The classical Coulomb energy,  $0.5e^2/R$  is obtained from second-order terms ( $\delta n^2$ ) in the expansion of  $E[n + \delta n]$  in  $\delta n$ , and does not appear in the chemical potential. The results of Table II also indicate that the magnitude of the deviation of  $I(R)$  from its classical value is not determined by a single term in the energy functional as proposed by EP,<sup>6</sup> but rather in a delicate balance between the various terms. The observation of these authors that the presence of the gradient terms in the kinetic energy is necessary for the existence of this effect is of course correct.

The results of the present calculation [and of Ref. 3(a)] are close to that inferred from observed ionization potentials of alkali, copper, and silver clusters.<sup>2</sup> Remaining deviations may be due to terms missing in the energy functional (5). This result is also close to that of image theory<sup>4</sup> which yields Eq. (1) with  $C = 3/8$ . This raises the question of whether the image theory result is just another manifestation of the quantum effects discussed above. This seems unlikely, as the image potential is a nonlocal exchange correlation phenomenon,<sup>9</sup> whereas our calculation considered only local effects. Furthermore, as we have shown before,<sup>3(a)</sup> the application of the image potential argument to the calculation of the ionization potential of a cluster characterized by a finite dielectric constant leads to diverging results. For these reasons we believe that agreement between the image theory result and the observed asymptotic behavior of the ionization potential in some clusters is probably accidental.

Finally we discuss two other implications of the present results.

TABLE I. Size dependence of the chemical and ionization potentials of jellium spheres (in a.u.).

$r_s$ ( $a_0$ )	$WF$	$\mu(\infty)$	$C$	$C_\mu$	$WF^a$	$C^a$	$\mu(\infty)^b$	$C_\mu^b$
2	0.118	–0.124	0.44	0.08	0.133	0.42	–0.125	0.072
4	0.098	–0.098	0.43	0.05	0.106	0.40	–0.099	0.082
6	0.082	–0.082	0.42	0.06	0.085	0.38	–0.079	0.075

<sup>a</sup>Variational calculation for jellium spheres Ref. 5.

<sup>b</sup>Obtained from direct solution of the Euler equation (Ref. 6).

TABLE II. Contributions of different energy terms to the chemical and ionization potentials and to their size dependence parameters  $C$  and  $C_\mu$  (in a.u.).

	$T_0$	$T_2$	$E_x$	$E_c$	$U$	Total
IP	-0.032	0.020	0.075	0.031	0.005	0.098
$C$	-0.12	-0.08	0.11	0.01	0.50	0.43
$\mu$	0.032	-0.020	-0.075	-0.031	-0.002	-0.098
$C_\mu$	0.13	0.10	-0.13	-0.02	-0.05	0.05

(a) Classical electrostatic theory yields the following expression for the charging energy of a metal sphere:

$$W = \frac{1}{2} \frac{Q^2}{R}, \quad (19)$$

where  $Q = Ze$  is the charge. This may seem incompatible with Eq. (1) if  $C \neq 1/2$ . To see how the classical limit (19) is obtained rewrite Eq. (1) in the form

$$I(R) = WF + \Delta E_q + \frac{1}{2} \frac{e^2}{R} = -\mu + \frac{1}{2} \frac{e^2}{R}, \quad (20)$$

where  $\Delta E_q = (C - 0.5)e^2/R$  represents the deviation from the classical behavior due to the quantum effects discussed above. Equation (20) corresponds to  $Z = 1$ . The energy needed to remove  $Z$  electrons from the spherical particle is accordingly

$$W(R) = -Z\mu + \frac{(Ze)^2}{2R}. \quad (21)$$

For large  $Z$  the last term dominates and we obtain the classical charging energy (19). Thus the classical limit is not obtained solely by considering a macroscopically sized sample but also by considering a macroscopic charge, i.e.,  $Z \gg 1$ .

(b) van Staveren *et al.*<sup>10</sup> have obtained an expression for the grand canonical ensemble average of the net charge  $\Delta N$  on a cluster of radius  $R$ ,

$$\Delta N = \frac{R}{e^2} (WF - \Delta E_q + \mu). \quad (22)$$

These authors assumed that the chemical potential is size independent and equal to  $-WF$ , and have pointed out that Eq. (22) leads to the peculiar result that at equilibrium the particles carry a net average charge of  $-e/8$ . However, if we accept that  $C + C_\mu = 0.5$ , as argued above, we get  $WF + \Delta E_q + \mu = 0$  for all cluster sizes, thus resolving the apparent paradox.

In summary, we have considered the asymptotic (large

$R$ ) dependence of the ionization potential and the chemical potential of spherical metal clusters. We have shown that a simple variational local-density-functional theory accounts semiquantitatively for the deviation of the ionization potential from its classical limit. The classical limit is obtained for large  $R$  and large charge  $Q$  ( $Q/e \gg 1$ ). The agreement of the image theory result with the quantum correction discussed here, and with the experimental results, is probably accidental.

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- <sup>8</sup> Strictly speaking  $n(r)$  should have a continuous first derivative for the gradient expansion expression (5f) to be valid to first order.  $n(r)$  of Eq. (17) does not satisfy this requirement at the jellium surface. However, for the parameters  $k$  and  $\lambda$  found here we have  $|n'(R_+) - n'(R_-)|/0.5[n'(R_+) + n'(R_-)] \approx |1 - k/\lambda| < 0.03$  so the error due to this discontinuity is negligible.
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