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Bulk-plasmon contribution to the work function of metals

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Abstract

By consideration of the Koopmans theorem expression for the work function of a metal, we find that the total height of the surface barrier potential equals the value of the bulk-plasmon energy of pure metals. As a consequence a simple formula for the work function is obtained which shows better agreement with the experimental data than the most complete existent theories.

The work function of metals is defined as the minimum energy needed to remove one electron out of the metal. This definition has been formally implemented in several ways [1–4], the most usual one being the expression considered by Lang and Kohn (LK) [1, 2] in their study of metal surfaces. It is given by

$$\Phi = \Delta\phi - \bar{\mu} \quad (1)$$

with $\Delta\phi$ the rise in mean electrostatic potential across the surface and

$$\bar{\mu} = E_F + \mu_{xc}(\bar{n}) \quad (2)$$

the relative bulk chemical potential of the electrons in the metal, with E_F the Fermi energy and $\mu_{xc}(\bar{n})$ the exchange and correlation part of the chemical potential for an infinite uniform electron gas of constant density \bar{n} within the local-density approximation. Since a closed expression for Φ has not been obtained yet its evaluation for metals has to be performed numerically [2–6].

Equation (1), also called the Koopmans theorem expression for the work function of metals [3, 4], considers $\Delta\phi$ and $\bar{\mu}$ as basic variables. It is also possible to rewrite it in terms of an alternative pair of variables which, as we shall see later, are better suited for the purposes of evaluating and interpreting Φ . Indeed, from equations (1) and (2) it is straightforward to write

$$\Phi = U_{xc} - E_F \quad (3)$$

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where the new variable U_{xc} , defined as

$$U_{xc} \equiv \Delta\phi - \mu_{xc} = \Delta\phi + |\mu_{xc}|, \quad (4a)$$

represents the total height of the surface barrier potential [4, 7]:

$$U_{xc} = v_{\text{eff}}(\infty) - v_{\text{eff}}(-\infty). \quad (4b)$$

By consideration of the original results reported by Lang and Kohn [2] for the quantities E_F , μ_{xc} , $\bar{\mu}$ and $\Delta\phi$, and for the metallic range $2 \leq r_s \leq 6$ of the Wigner–Seitz radius, we note that

- (i) μ_{xc} is negative in the whole range of r_s under consideration so that the summation in equation (2) turns into a subtraction which is responsible for the strong internal cancellations of $\bar{\mu}$ and for its change of sign. In fact, for $r_s = 2.5$ the magnitude of $\bar{\mu}$ is only a few per cent of both E_F and $\mu_{xc}(\bar{\mu})$.
- (ii) $\Delta\phi$ suffers very strong variations within the metallic range in such a way that the relative importance of $\Delta\phi$ and $\bar{\mu}$ changes drastically as r_s varies. For instance, for $r_s = 2.5$, $\Delta\phi$ is more than 30 times larger than $|\bar{\mu}|$, while for $r_s = 6.0$ the value of $\Delta\phi$ is only 1.7% that of $|\bar{\mu}|$.
- (iii) It is obvious from equation (4a) that U_{xc} will not suffer internal cancellations, with its range of variation (a factor of 5) being much smaller than that of $\Delta\phi$ (a factor of 170). Furthermore, application of the results of Lang and Kohn in equation (4a) yields U_{xc}^{LK} whose values are always larger than E_F and with a slower decay as function of r_s , although E_F never gets negligible as compared to U_{xc}^{LK} .

Therefore, within the context of the density-functional calculations [1, 2], we conclude that U_{xc} and E_F present a much more desirable behaviour than $\Delta\phi$ and $\bar{\mu}$ as basic variables to describe and to evaluate the work function of metals. Furthermore, in this work we obtain the following fundamental result: *for pure metals the value of U_{xc} equals the value of the corresponding bulk-plasmon energy*. As an immediate consequence a very simple and closed formula for the work function of metals is obtained, as a function only of the Wigner–Seitz radius r_s , which yields to an agreement with the experimental data for simple metals (and also for more complex ones) which is better than that obtained with any of the most recent approaches [4–6].

We proceed noting first that, in terms of r_s , the Fermi energy is given by the simple power-law expression [8] $E_F = 50.1r_s^{-2}$ (eV). On the other hand, as already mentioned, U_{xc}^{LK} has a slower decay than E_F , it being a simple matter to verify that it decays more quickly than the exchange potential μ_x which is well known [2] to have a r_s^{-1} behaviour. From this fact one wonders if U_{xc}^{LK} can be described within a reasonable approximation by a simple relation of the form Ar_s^{-p} , with A and p constants and with $1 < p < 2$. A useful hint in seeking an answer to this question comes from an earlier work by Gutierrez [9], who found that the ionization potential for the last bound s state of hydrogen-like ions, immersed in a finite temperature electron gas and described by an exponentially screened Coulomb (‘Debye–Huckel’) potential [10], is close to the bulk-plasmon energy $E_{\text{pl}} = \hbar\omega_p$ (with $\omega_p = \sqrt{4\pi\bar{n}}$ in au) of the electron gas. Such a strong relationship between the last bound s state of screened potentials and the plasma oscillations comes as a result of an approximate matching between the minimum plasmon wavelength and the size of the last bound orbit which is valid at all densities.

It is straightforward to show that a similar result applies for an ion of charge Z immersed in the degenerate electron gas of metals by consideration of a short-range screened Coulomb potential [11, 12] with the screening length equal to the minimum bulk-plasmon

wavelength [12, 13]⁴. In this case the ratio R of the bulk-plasmon energy to the binding energy of the last bound s state of the screened Coulomb potential is approximately given by⁵ (with E_F in eV)

$$R \approx 1.83 \sqrt{\frac{E_F}{Z^2(Z+1)}} \quad (5)$$

which depends on density as $n^{\frac{1}{3}}$ (or equivalently as r_s^{-1}). As an illustration let us consider the core-ions of three metals: Na, Mg and Al with [8] $Z = 1, 2$ and 3 and $E_F = 3.24$ eV, 7.08 eV and 11.7 eV, respectively. Therefore from equation (5) one gets for R the values 2.33 , 1.41 and 1.04 respectively, which we take as a signature of a strong connection between the collective fields and the last bound level of each ion-core. Indeed, taking the minimum plasmon wavelength [12, 13] as the screening length for the short-range screened Coulomb potential of the core-ions under consideration yields [10] in each case a value of $n = 2$ for the last allowed hydrogen-like bound state, which happens to coincide with the last bound shell for the core-ions of the three metals.

The above ideas can be qualitatively extended to pure metals if one considers the conduction band as the ‘last bound shell’ of the metal with its bottom playing the role of the ‘ s state’ since it corresponds to the lowest energy level within the band. Thus, in this case one should compare the height of the surface barrier potential U_{xc} , given by equation (4a), with the bulk-plasmon energy of each metal. In fact for the metals Na, Mg and Al the sum $E_F + \Phi$ gives [8] (in eV) 5.94 , 10.72 and 15.95 , which compares pretty well with the corresponding bulk-plasmon energy values 6.04 , 10.89 , and 15.78 respectively (with a relative error below 1.6%). More importantly, the bulk-plasmon energy can be rewritten in terms of r_s as $E_{pl} = 47.1r_s^{-3/2}$, showing an r_s dependence which is consistent with the above-mentioned possible behaviour of U_{xc} .

The previous discussion points to a strong connection between U_{xc} and the energy of bulk plasmons. Therefore in figure 1 we compare the behaviour of U_{xc}^{LK} , E_{pl} and E_F as functions of r_s . Although for high densities (small r_s) the values of U_{xc}^{LK} stay close to the E_{pl} curve, this approximate agreement is lost at low densities (larger values of r_s), so we cannot interpret directly U_{xc}^{LK} as the energy of bulk plasmons for the metal. However, we should note that U_{xc}^{LK} corresponds only to an approximation (LDA) to the correct behaviour of U_{xc} (as a function of r_s). On the other hand, we note from equation (3) that, since for the electron gas E_F is a well-defined function of r_s , measurement of Φ should give us direct information about U_{xc} through the relation

$$U_{xc}^{Exp} = \Phi^{Exp} + E_F. \quad (6)$$

Therefore in figure 2 we compare the bulk-plasmon energy E_{pl} with the total height of the surface barrier potential U_{xc}^{Exp} which has been evaluated with the experimental data for the work function Φ^{Exp} of 21 metals obtained from [14–16]. Those values in filled squares (labelled Exp.1) correspond to simple metals (five s metals Li, Na, K, Rb, Cs, plus four p metals Al, Ga, In, Tl), while empty squares (Exp.2) correspond to another twelve elements (the s^2 metals Be, Mg, Ca, Sr, Ba; the $d^{10}s^2$ metals Zn, Cd, Hg; the s^2p^2 metals Sn, Pb, and the s^2p^3 metals Sb and Bi). We note that in the literature [8, 15] we have found three different experimental values for the work function of Be ($r_s = 1.87$). In figure 2 we have included the corresponding U_{xc}^{Exp}

⁴ The minimum bulk-plasmon wavelength is taken as the inverse of the maximum plasmon wavevector k_c allowed by Bohm–Pines theory of [12, 13]. The value of k_c is chosen as the one that minimizes the ground-state energy of the system.

⁵ The average energy per particle $3k_B T/2$ for the electrons in the finite-temperature plasma must be replaced by the average energy per particle $3E_F/5$ of the degenerate electron gas.

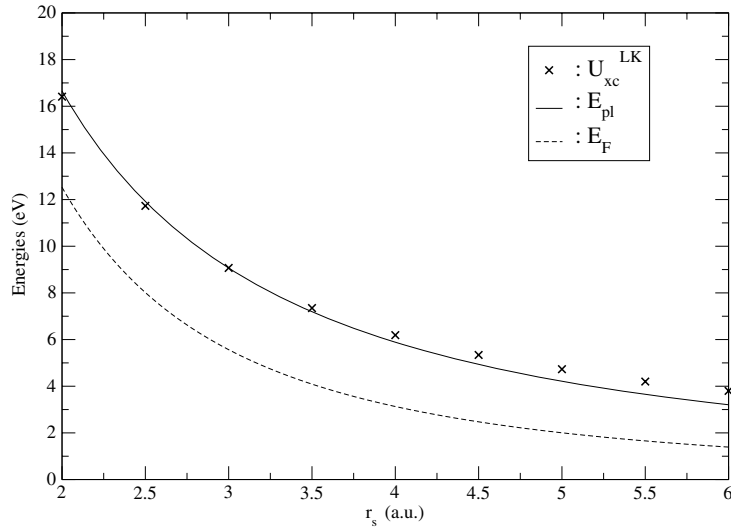


Figure 1. Energies (eV) as functions of the Wigner–Seitz radius r_s (au). \times : U_{xc}^{LK} ; full line: the bulk-plasmon energy E_{pl} ; dashed line: the Fermi energy E_F .

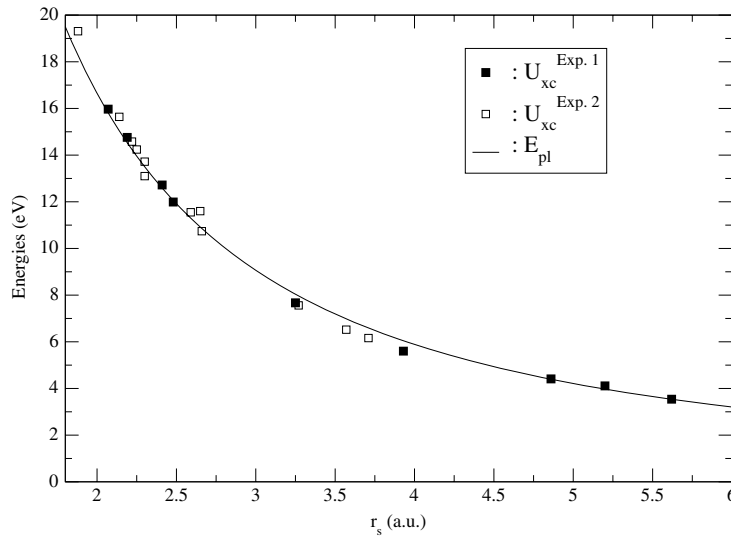


Figure 2. Energies (eV) as functions of the Wigner–Seitz radius r_s (au). \blacksquare : $U_{xc}^{Exp.1}$ corresponding to the nine polycrystalline simple metals of columns 1 and 13 of the periodic table (Al, Ga, In, Tl, Li, Na, K, Rb, Cs for increasing r_s values); \square : $U_{xc}^{Exp.2}$ corresponding to 12 polycrystalline more complex metals of columns 2, 12, 14 and 15 of the periodic table (Be, Sb, Sn, Bi, Pb, Zn, Cd, Hg, Mg, Ca, Sr, Ba for increasing r_s values); full line: the bulk-plasmon energy E_{pl} .

value which is farthest from the E_{pl} curve, the other two values being closer to it. The overall agreement between the U_{xc}^{Exp} values and the bulk-plasmon energy curve (E_{pl}) is astonishing. Indeed, we obtain 3% for the average relative error between the E_{pl} curve and the 21 values of U_{xc}^{Exp} reported in figure 2. Therefore, we conclude that, for the range of metallic densities

$$1.87 \leq r_s \leq 6,$$

$$U_{xc} = \hbar\omega_p = \frac{47.1}{r_s^{3/2}} \text{ (eV)}, \quad (7)$$

so for pure metals the total height of the surface barrier potential is completely defined by the energy of the corresponding bulk plasmons. This statement comes as an experimental fact which is independent of the way it has been obtained. We believe that it might have strong consequences for the whole area of metal surface physics.

Perhaps equation (7) should not be too unexpected since it is already known [7] that the total height of the surface barrier potential is mostly a bulk property, this being the reason why it is not too much affected by the local-density approximation in the surface region. Two related comments follow. (i) Within the Bohm–Pines collective description of electrons in metals [11, 12]—modelled as a sea of weakly interacting screened electrons plus a set of bulk plasmons which account for the long-range part of the Coulomb interaction—Pines [13] obtained a correlation energy in reasonable agreement with the classical result of Wigner but with the exchange energy greatly reduced by the long-range correlations. In this scheme if one takes an electron from the bottom of the conduction band of the metal out to infinity the screening of the electron fields should render the single-particle response of the metal negligible as compared to its bulk-plasmon response. (ii) In calculations of transition rates for ion neutralization at metal surfaces [17] it has been found that when an external ion, at intermediate or large distances from the metal, captures an electron from the metallic surface the solid is more willing to accept the surplus energy (given up by the captured electron in going from the conduction band of the solid to the low-lying atomic level of the external ion) through a collective response than through a single-particle response, something which is confirmed by dielectric response calculations [18], in which it is found that for intermediate and large distances it is the collective response of the metal which determines the neutralization rate of the ions. Although surface plasmons are considered in [17, 18], an equivalent analysis for an electron removed from the interior of the metal would give rise to bulk plasmons. Incidentally, it has been mentioned [19], in connection with the Thomas–Fermi–von Weizsacker approach for the metallic surface, that the relevant equations are most easily solved if one uses the variable $[n(x)]^{1/2}$ instead of $n(x)$ since the system becomes somehow less unstable. Perhaps this situation is another sign of a plasmon-like ordering of the electron gas.

An immediate consequence of equation (7) is to yield a simple closed expression for the work function of metals as

$$\begin{aligned} \Phi^{\text{GDJ}} &= U_{xc} - E_F \\ &= \left(\frac{47.1}{r_s^{3/2}} - \frac{50.1}{r_s^2} \right) \text{ (eV)}. \end{aligned} \quad (8)$$

In figure 3(a) the work function Φ^{GDJ} is compared with both the corresponding theoretical curve of Lang and Kohn [2] and the experimental data for the same set of metals considered by them. The experimental values for these metals have been updated with the information given in [14–16]. It is clear that Φ^{GDJ} is in better agreement with the experimental values than the LK curve. In particular for Al, (a typical ‘electron gas metal’), equation (8) yields a workfunction of 4.13 eV, which compares pretty well with the experimental value of 4.28 eV but clearly differs from the LK result (3.87 eV). More than that, Φ^{GDJ} is able to follow the general structure shown by the experimental data: changes of slope with a maximum at $r_s = 2.01$ corresponding to an electron density slightly greater than that of Al ($r_s = 2.07$). This structure is completely absent in the curve of Lang and Kohn which is practically a straight line with negative slope within the metallic range.

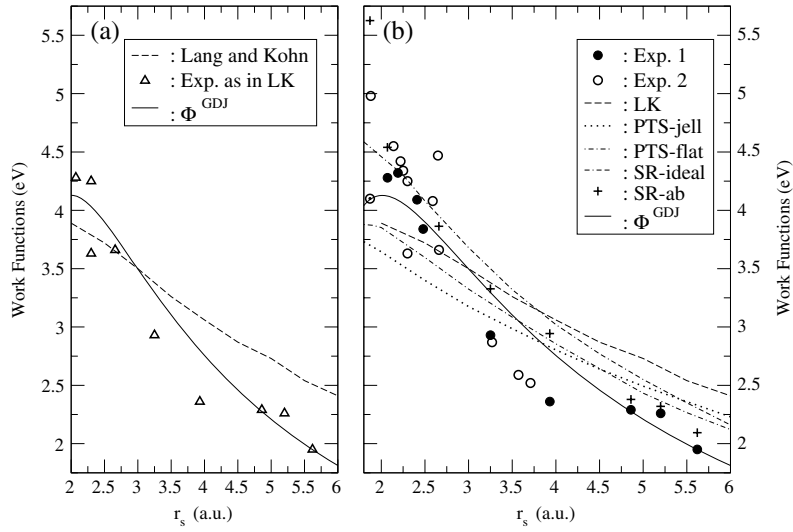


Figure 3. Work functions (eV) as functions of the Wigner–Seitz radius r_s (au). (a) Dashed line: the Lang and Kohn result [2]; \triangle : the more recent experimental results for the nine polycrystalline metals considered by Lang and Kohn (Al, Pb, Zn, Mg, Li, Na, K, Rb, Cs for increasing r_s values); full line: Φ^{GDJ} . (b) \bullet : experimental data for the same nine simple elements already considered in figure 2; \circ : experimental results for the 12 more complex metals already considered in figure 2. Dashed line: the Lang and Kohn result [2]; dotted line: the Perdew *et al* result [4] (jellium); dot-dashed line: the Perdew *et al* result [4] (pseudopotential); dotted–double dashed line: the Shore and Rose result [5]; +: the Skriver and Rosengaard result [6]; full line: Φ^{GDJ} .

In figure 3(b), Φ^{GDJ} is compared with the most relevant theoretical results, besides those of Lang and Kohn, that we have found so far in the literature. They correspond to the results of Perdew, Tran and Smith [4] for both the jellium model (PTS-jell) and the flat surface structureless pseudopotential model (PTS-flat) (which they indicate has an estimated numerical error of 0.02 eV for $r_s \geq 1$), the results of Shore and Rose [5] for their ideal metal model (SR-ideal), and the results of Skriver and Rosengaard [6] for their *ab initio* calculations (SR-ab). Finally, in figure 3(b) we also include the experimental work functions for the same metals already considered in figure 2. Filled circles correspond to the work function of Li, Na, K, Rb, Cs, Al, Ga, In and Tl, while with empty circles we represent the experimental results for the other 12 metals (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, Pb, Sb and Bi) [14–16]. For Be (at $r_s = 1.87$) we have included the two different values for the experimental work function (4.10 eV, dotted circle and 4.98 eV, empty circle) obtained from [15]. In [8] they indicate a value of 3.92 eV for the same metal which is not included here. For the simple metals (filled circles) we see that the Φ^{GDJ} curve follows the trend of the experimental data better than the other theoretical curves. In order to have a quantitative measure of how close each theoretical curve is to the experimental points we have computed the average relative error $\tilde{\Delta}$ inherent to each curve (or set of points as in the SR-ab case) as

$$\tilde{\Delta} \equiv \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \frac{|\Phi_{\text{th}}([r_s]_i) - \Phi_{\text{exp}}([r_s]_i)|}{\Phi_{\text{exp}}([r_s]_i)} \quad (9)$$

where N_{exp} is the number of experimental points considered for the calculation of $\tilde{\Delta}$ while $\Phi_{\text{th}}([r_s]_i)$ and $\Phi_{\text{exp}}([r_s]_i)$ are respectively the theoretical and experimental values of the work

Table 1. Average relative errors $\tilde{\Delta}$ (in %) between the experimental work functions values and the theoretical results considered in this work (see text and equation (9)).

N_{exp}	LK	PTS-jell	PTS-flat	SR-ideal	SR-ab	GDJ
9	16.1	13.7	11.0	11.4	7.6	5.8
21	15.2	15.2	12.8	11.0	9.5	8.8

function. The corresponding $\tilde{\Delta}$ values calculated for the nine simple metals of figure 3(b) and also for the whole set of experimental data ($N_{\text{exp}} = 21$) considered in this work are reported in table 1. In both cases the average relative error related to Φ^{GDJ} is the smallest one⁶. Moreover, from table 1 we note that in both calculations the general situation does not change very much among the theories, although when all the metals are considered there is less agreement between theories and experiments, as expected. From figure 3(b) we also note that only the PTS-flat curve contains some weak structure, although the changes of slope are much less pronounced than those present in Φ^{GDJ} , especially at high densities where it gives too low values for the work function. On the other hand the SR-ab results stay close to the Φ^{GDJ} curve for the range $r_s \gtrsim 2.5$. For higher densities the SR-ab results are larger than both Φ^{GDJ} and the experimental ones, without showing a maximum. In that way the SR-ab average relative errors are slightly greater than the GDJ ones (see table 1). Finally, the SR-ideal curve overestimates the work functions of most simple metals, being very close to the experimental data in the restricted region of densities $2 < r_s < 2.5$ but too high at intermediate and low densities.

We should emphasize the fact that the empirical result of equation (8) is expected to be valid strictly within the range $1.87 \leq r_s \leq 6$ which corresponds to typical metallic densities. It might not be valid for other values of r_s . In fact, from equation (8) one finds that the work function vanishes at $r_s = 1.11$, becoming negative for smaller r_s values, which corresponds to a completely unphysical behaviour. However, in the case of metallic hydrogen obtained at extremely high pressures [20] the value $r_s = 1.58$ has been considered [4], which yields $\Phi^{\text{GDJ}} = 3.65$ eV, while from the work of Perdew and Wang [21] (exchange and correlation included) one gets a value of 3.80 eV, which differs from our result by less than 4%. Therefore, for large but realistic densities Φ^{GDJ} might still be approximately valid. On the other hand, since for low densities within the typical metallic range Φ^{GDJ} represents the experimental data much better than the other theories and since all the curves in figure 3(b) show a smooth behaviour, we might expect that this situation will be maintained for very low densities. In particular, for $r_s = 12$ our formula yields $\Phi^{\text{GDJ}} = 0.79$ eV, while Perdew and Wang [21] obtained 1.34 eV. In conclusion, a very simple and closed expression for the work function of metals has been given, in terms of two fundamental quantities namely the bulk-plasmon energy and the Fermi energy, which happens to yield results which agree with the experimental data better than those obtained with any other existent theory.

Acknowledgments

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⁶ We obtain the same conclusion by computing the standard deviation instead of the average relative error.

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