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L U B L I N – P O L O N I A

Comment on 'Bulk-plasmon contribution to the work function of metals'

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ABSTRACT

Simple derivation of work function of metals based on the bulk-plasmon contribution is discussed here in a form of a comment to previously published work. We show that such a derivation is neither the first of its kind, nor it is in agreement with experimental data. Incidentally, the physical foundations of the proposed derivation appear to be flawed.

In their paper [1] F.A. Gutierrez and collaborators describe a way of calculating work function (WF) of metals from the bulk-plasmon contribution. The total surface barrier potential is assumed to be equal to the bulk-plasmon energy, and the Koopman's theorem is rewritten from a function of mean electrostatic potential and bulk chemical potential, to a function of Fermi energy and the total height of the surface barrier potential. Fermi energy is expressed within the Sommerfeld model as a function of Wigner-Seitz radius, r_s. Next, the bulk-plasmon energy is expressed in terms of r_s and hence work function is calculated as a function of r_s only. Authors claim the following:

– evaluations of work function for metals were so far performed numerically, and closed expression for work function is proposed for the first time;

– proposed theory is expected to be valid within the range $1.87 \leq r_s \leq 6$;

– proposed theory produces results in better agreement with experimental data than in the case of any other theory proposed so far;

– total surface barrier potential is equal to bulk-plasmon energy.

In our view, all above claims are incorrect.

Authors seem unaware of a vast body of work devoted to expressing work function of metals in terms of electron density in the form of a closed expression.

One of the first papers on contribution of free electrons in metal to its work function was published in 1978 [2], where authors calculated the WF values for 26 metals by using the hydrodynamic model of Bloch and Thomas-Fermi approximation to derive a closed expression for work function, proportional to $r_s^{-1/2}$. Another example comes from Brodie [3], who reduced WF to work done by an electron against the image forces, and expressed WF as a function of atomic radius, Fermi energy and effective mass of the electron, providing values for 8 metals and four absorbate systems. Finally, in our own work [4, 5] we improved Brodie's approach by using the length of spontaneous polarization of the electron gas at the Fermi level to express WF as a sole function of r_s and calculate its value for a total of 80 elements: simple metals, transition metals, lanthanides and actinides. One could show many more examples of closed expression approaches to WF published within the last 30 years, and specifically to expressing this property solely as a function of density.

Regarding the range of applicable r_s, authors point out that their formula predicts a maximum in WF around $r_s = 2.01$ and diminishing values of WF below this point, reaching zero around $r_s = 1.11$.
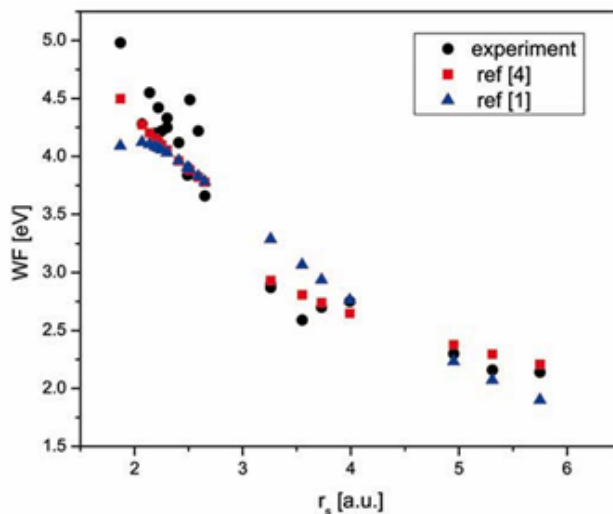

Fig. 1. Comparison of experimental work function values as a func-tion of electron density parameter with simple theory presented in refs [1] and [4].

As authors note, this behaviour is completely unphysical. Metals like Be, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Ir, Ni, Pt, U and Np all have $r_s \leq 2.01$. For example,

in the case of Pt the author's curve predicts WF = 4.10 eV, while the experimental value is 5.65 eV and calculated in [4] is 5.55 eV, corresponding to an underestimation by 1.55 eV by the authors. In the case of Ir and Ni, the underestimations are 1.18 eV and 1.04 eV, respectively. The previously suggested diminishing of WF for high electron density materials [6], including a two-peak structure has never been observed experimentally and is most likely an unphysical artifact of the calculation, just like in the case of the paper discussed here.

Contrary to the authors' claim, agreement with experimental values over a broader range of r_s is also not impressive. Authors perform comparison between 5 different theories and their own for a selection of 21 metals, in a way almost identical to what was done in [5] for 16 theories (or theory flavours). By calculating the average relative error in a way suggested by authors in [1] for the same 21 metals, we obtain 7.75 percent for their work and 4.75 percent using data from [4]. Comparison between [1] and [4] and experimental data is shown in Figure 1. As it can be seen, WF values calculated in [1] are too low in the high density range, too high in the mid-density range and again too low in the low electron density range.

In conclusion, authors of [1] describe a work function calculation method that is neither the best nor the first of its kind. In terms of number of elements and agreement with experiments it falls far behind previously published work.

The fundamental reason for this discrepancy is an erroneous assumption that total surface barrier potential is equal to bulk-plasmon energy. The two functions, as well as the Fermi energy, are indeed related through electron density and have a similar form. This would explain why the calculated values of work function fall in the vicinity of the experimental values. But the bulk-plasmon energy traces the Fermi energy, which is a bulk property. Bulk-plasmons are not related to the surface barrier potential, which is a surface property. The relationship between Fermi energy and bulk-plasmon energy comes from the fact that plasmon excitations may occur on the cost of Fermi energy, but not on the cost of surface barrier potential. We therefore conclude that all similarity of the WF values calculated by formula (8) in discussed paper to experimental values is fortuitous, but unfortunately not physical.

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