COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on ''Uncertainty, topography, and work function''

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In his paper [Phys. Rev. B **51**, 13 660 (1995)], Brodie gives a very interesting and simple method of calculation of work function of planar surfaces. However, he makes a few errors in derivation of the formula for the Schottky effect, which are discussed and verified in this Comment. The corrected procedures of calculation of the Schottky effect according to Brodie's idea are given.

Brodie's[1] novel approach to the work function (WF) calculation without use of the *ab initio* methods was used by numerous researchers[2] and it was substantially improved most recently.[3] His concept is based on the image force calculations for an electron leaving a surface of spherical geometry. Real surface is represented by an array of spheroids. Integration of the image force acting on an electron is performed to obtain WF. Integration limits are d and infinity, where d is a certain distance from the surface, calculated from uncertainty principle.

In his paper, Brodie[1] demonstrates the applicability of his approach by calculation of the magnitude of lowering of the work function in presence of external electric field of appriopriate direction, recognized as the Schottky effect.[4] He derived the following equations for the image force, F_C, and electric field force, F_E, acting on an electron in the vicinity of the sphere of radius R:

$$F_C=\frac{e^2}{4\pi\varepsilon_0}\frac{R(R+x)}{[(R+x)^2-R^2]^2},$$

$$F_E=eE_0\frac{R^2}{(R+x)^2},$$

where ε_0 is vacuum permittivity, x is distance from the surface, and E_0 is the electric field at the surface of the sphere. One should keep in mind that the signs of acting forces are opposite. To find the WF of a planar surface in absence of external fields one should integrate the image field force, $e\varphi=\int_d^\infty F_C dx$, and find the limit of obtained expression for $R\rightarrow\infty$. In presence of an external electric field, there is a certain distance, $x_0>d$, at which the sum of the two forces, acting in opposite directions, equals zero. This distance may be found by solving the $|F_C|=|F_E|$ equation. Brodie proposes to solve this equation assuming that $R\rightarrow\infty$, which radically simplifies the calculation and yields a value of $x_0=\frac{1}{4}\sqrt{e/\pi\varepsilon_0 E_0}$. In the presence of an external field Brodie proposes to calculate WF as

$$e\varphi'=\int_d^{x_0}F_C dx+\int_0^{x_0}F_E dx. \tag{1}$$

Image force is integrated to x_0, which is the distance from the surface of a sphere to the point where $|F_C|=|F_E|$.

The error made by Brodie is that the F_E force should not be integrated from 0. It was one of the foundations of Brodie's approach that the electron at distances from the surface smaller than d are subjected to ''continuous decoherence from quantum states at the first boundary to classical states at the second'' (Ref. 1), where ''the second'' boundary is d. According to this point of view, the electron below a distance d from the surface of the sphere may not be described by classical methods, as it is done in formula (1). The application of the uncertainty principle is proposed by Brodie for planar surfaces in the absence of electric fields and should be used consequently in presence of external fields. Therefore, the corrected formula (1) should be

$$e\varphi'=\int_d^{x_0}F_C dx+\int_d^{x_0}F_E dx. \tag{2}$$

The Schottky lowering of WF is given by Brodie as

$$\Delta(e\varphi)=\int_d^\infty F_C dx-\int_d^{x_0}F_C dx-\int_0^{x_0}F_E dx$$
$$=\int_{x_0}^\infty F_C dx-\int_0^{x_0}F_E dx.$$

By integration of the above erroneous formula, Brodie obtains his formula (13) for Schottky lowering,

$$\Delta(e\varphi)=\frac{e^2}{4\pi\varepsilon_0}\frac{R}{(R+x_0)^2-R^2}-eE_0R^2\left[\frac{1}{R}-\frac{1}{R+x_0}\right], \tag{3}$$

and commits three mistakes. First, the correct value of $\int_{x_0}^\infty F_C dx$ is

$$\frac{e^2}{8\pi\varepsilon_0}\frac{R}{(R+x_0)^2-R^2},$$

being half of the value in Brodie's formula (13). The ''+'' sign should be taken instead of ''−'' before the second term, because the forces F_E and F_C act in opposite directions. Brodie states also that ''as R tends to infinity, the first term [of the above formula] tends to the conventional Schottky relation ... and the second term tends to zero, as expected.'' This is not the case. The second term, namely,

$$eE_0R^2\left[\frac{1}{R}-\frac{1}{R+x_0}\right],$$

tends to eE_0x_0 instead of zero, as R tends to infinity. Taking into account the three errors listed above, the corrected calculations for $R\rightarrow\infty$ are

$$\Delta e\varphi=\frac{e^2}{8\pi\varepsilon_0}\frac{R}{(R+x_0)^2-R^2}+eE_0R^2\left[\frac{1}{R}-\frac{1}{R+x_0}\right]$$

$$=\frac{e^2}{8\pi\varepsilon_0}\frac{1}{2x_0+x_0^2/R}+eE_0\frac{x_0}{1+x_0/R}$$

$$\rightarrow\frac{e^2}{16\pi\varepsilon_0x_0}+eE_0x_0.$$

By substituting, after Brodie,

$$x_0=\frac{1}{4}\sqrt{\frac{e}{\pi\varepsilon_0E_0}}$$

we obtain

$$\Delta e\varphi=\sqrt{\frac{eE_0}{16\pi\varepsilon_0}}+\sqrt{\frac{eE_0}{16\pi\varepsilon_0}}=\sqrt{\frac{eE_0}{4\pi\varepsilon_0}}$$

which is a conventional Schottky relation, valid for very large R values and $x_0\gg d$. To obtain the real values of Schottky lowering for spherical geometry by use of Brodie's approach one should (i) calculate x_0 by solving equation $|F_C|=|F_E|$, rejecting the complex solutions and choosing this one of the two real solutions which is larger than d, and (ii) calculate $\Delta e\varphi$ by use of the correct formula (2) from this Comment instead of Brodie's formula (12):

$$\Delta e\varphi=\int_{x_0}^{\infty}F_Cdx-\int_{d}^{x_0}F_Edx. \tag{4}$$

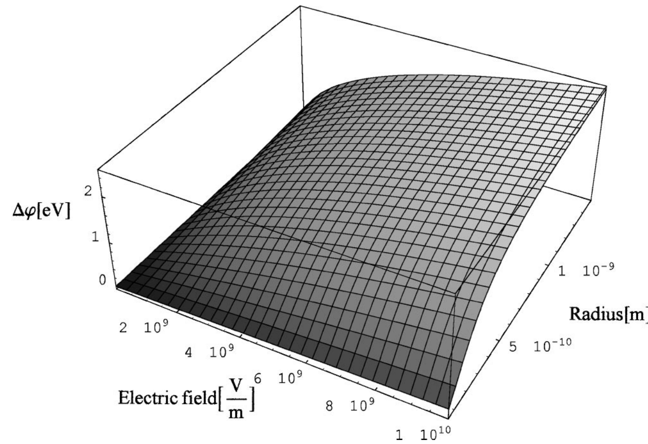

FIG. 1. Plot of the Schottky lowering (eV) calculated according to formula (4) for an electric field varying from 1 to 10^{10} V/m and a sphere radius varying from 0.5 to 15 Å.

The correct solution for $R\rightarrow\infty$ is

$$\Delta e\varphi=\frac{e^2}{16\pi\varepsilon_0x_o}+eE_0(x_0-d).$$

For planar surfaces we may substitute Brodie's solution, $x_0=\frac{1}{4}\sqrt{e/\pi\varepsilon_0E_0}$, in the equation above and find the Schottky lowering as follows:

$$\Delta e\varphi=\sqrt{\frac{eE_0}{4\pi\varepsilon_0}}-eE_0d.$$

The traditional Schottky relation predicts a slightly larger value. Penetration of electrons, extending beyond the geometric surface,[5] seems to be successfully described by including the d value into calculations. Obtaining values of Schottky lowering for any R is possible only if x_0 is obtained by numerical solving of $|F_C|=|F_E|$ equation. Results obtained by use of formula (4) are shown in Fig. 1.

It has to be noted that the main concept of WF introduced by Brodie is very interesting. The necessary correction of errors allows us to demonstrate the general applicability of the Brodie's approach.

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[1] I. Brodie, Phys. Rev. B **51**, 13 660 (1995).

[2] D.J. Klinke, S. Wilke, and L.J. Broadbelt, J. Catal. **178**, 540 (1998); K.F. Wojciechowski and H Bogdanow, Surf. Sci. **397**, 53 (1998); K.F. Wojciechowski, J. Chem. Phys. **108**, 816 (1998); Vacuum **48**, 257 (1997); Europhys. Lett. **38**, 135 (1997); Vacuum **48**, 891 (1997); B. Barwinski and S. Sendecki, *ibid.* **47**, 1479 (1996).

[3] S. Halas and T. Durakiewicz, J. Phys.: Condens. Matter **10**, 10 815 (1998).

[4] W. Schottky and C. A. Hartmann, Z. Phys. **2**, 206 (1920).

[5] A. Kiejna and K. F. Wojciechowski, *Metal Surface Electron Physics* (Elsevier Science, Oxford, 1995).