
COMMENTS AND ADDENDA

The Comments and Addenda section is for short communications which are not of such urgency as to justify publication in *Physical Review Letters* and are not appropriate for regular Articles. It includes only the following types of communications: (1) comments on papers previously published in *The Physical Review* or *Physical Review Letters*; (2) addenda to papers previously published in *The Physical Review* or *Physical Review Letters*, in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section may be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galley proofs will be sent to authors.

Surface-Dipole Barriers in Simple Metals

N. D. Lang

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

W. Kohn*

University of California, San Diego, La Jolla, California 92037

(Received 20 June 1973)

The uniform-charge-background (jellium) model of a bounded metal is shown to give good estimates of the electrostatic surface-dipole barriers in simple metals.

The uniform-charge-background (or jellium) model of a metal surface has been found to give a good account of the measured work functions Φ of simple metals.¹⁻⁵ Corrections to first order in the pseudopotential $\delta v(\vec{r})$ have also been calculated⁴ and found to be small.

Recently there has been a fair amount of interest⁶ in the electrostatic surface-dipole barrier $\Delta\phi$, often in connection with the study of the energy required to remove a positron from the metal. Here we wish to point out that, to first order in the perturbation $\delta v(\vec{r})$, the change of the dipole barrier $\delta(\Delta\phi)$, when properly defined, equals the change of the work function $\delta\Phi$, which we found earlier to be ≤ 0.5 eV in magnitude. Thus the uniform-background model also provides a rather accurate estimate of the dipole barriers $\Delta\phi$ of simple metals. Recent assertions to the contrary⁷⁻⁹ will be shown to be based on an incorrect comparison of dipole barriers defined in two different ways.

The electrostatic dipole barrier $\Delta\phi$, the work function Φ , and the bulk chemical potential $\bar{\mu}$, are quite generally related as follows⁴:

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

here

$$\Delta\phi \equiv \phi(+\infty) - \bar{\phi}, \quad (2)$$

where $\phi(+\infty)$ and $\bar{\phi}$ are, respectively, the electrostatic potential far outside the metal and the mean

electrostatic potential deep inside the metal; and $\bar{\mu}$ is the bulk chemical potential relative to the mean interior potential $\bar{\phi}$.

We shall now show that, to first order, the perturbation $\delta v(\vec{r})$ does not change $\bar{\mu}$ from its uniform background value:

$$\delta\bar{\mu} = 0. \quad (3)$$

Denoting quantities associated with the uniform-background model by the subscript u , the desired result,

$$\Delta\phi = \Delta\phi_u + \delta\Phi, \quad (4)$$

(again to first order in δv) will then follow immediately from Eq. (1).

In the theory of Hohenberg and Kohn¹⁰ there occurs the universal functional of the electron density $n(\vec{r})$ defined by (in atomic units):

$$G[n(\vec{r})] \equiv \langle \Psi | T + U | \Psi \rangle - \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}', \quad (5)$$

where Ψ is the electronic ground state and T and U are, respectively, the kinetic- and Coulomb-interaction-energy operators. The bulk chemical potential $\bar{\mu}$ relative to the mean interior potential $\bar{\phi}$ is given by¹¹

$$\bar{\mu} = \frac{1}{\Omega} \int_{\text{crystal}} d\vec{r} \frac{\delta G[n]}{\delta n(\vec{r})} \quad (6)$$

TABLE I. Electrostatic surface-barrier heights, as defined by Eq. (2), calculated for nine simple metals. $\Delta\phi_u$ is the barrier height computed in Ref. 4 for the uniform-background model; $\Delta\phi$ is this barrier height corrected to first order for the effects of the discrete-lattice pseudopotential. The pseudopotential core radii r_c employed were those given by Ashcroft and Langreth (Ref. 14) (in some cases these authors give two possible r_c values for a given metal). The barrier heights $\Delta\phi_{ws}$ and $\Delta\phi''$ are discussed in the text. The barrier height defined by Eq. (2) ($\Delta\phi$) is relatively insensitive to ambiguities in the pseudopotential, whereas the barrier height defined in Refs. 7-9 ($\Delta\phi'$ —see text) is sensitive to such ambiguities. This makes the comparison of $\Delta\phi$ and $\Delta\phi''$ in the Table difficult in some cases (e.g., Pb).

Metal	$\Delta\phi_u$ (eV)	r_c (a. u.)	$\Delta\phi$ (eV)			$\Delta\phi_{ws}$ (eV)	$\Delta\phi''$ (eV)
			(110)	(100)	(111)		
Al	6.2	1.12	6.0	6.6	6.4	2.4	5.8
Pb	4.8	1.12	4.8	4.9	4.8	4.7	5.0
		1.47	4.8	5.5	5.1	1.7	2.0
Zn	4.8	1.27	5.1 for (0001) face			0.2	3.1
Mg	3.3	1.39	3.7 for (0001) face			0.7	2.7
Li	1.8	1.06 ^a	2.0	1.7	1.6	1.2	2.4 ^a
Na	0.9	1.67	0.9	0.6	0.5	0.3	1.0
K	0.4	2.14	0.4	0	0	0.1	0.3
Rb	0.2	2.61	-0.2	-0.3	-0.4	-0.4	-0.3
		2.13	0.3	0	-0.1	0.3	0.4
Cs	0.1	2.93	-0.1	-0.5	-0.6	-0.5	-0.6
		2.16	0.2	-0.1	-0.2	0.4	0.3

^aTwo r_c values were given for Li in Ref. 4. Only the one which leads to a computed work function in agreement with recent measurements [V. K. Medvedev, A. G. Naumovets, and T. P. Smereka, Surface Sci. 34, 368 (1973) (high-coverage limits)] is retained here. Also, only that result for $\Delta\phi'$ from Ref. 7 which was based on this recent value (≈ 3 eV) was used to compute $\Delta\phi''$ for Li.

(Ω is the crystal volume). Now let $\delta v(\vec{r})$ be a small perturbing potential and let $\delta n(\vec{r})$ and $\delta\bar{\mu}$ be the corresponding changes of $n(\vec{r})$ and $\bar{\mu}$. Then, by Eq. (6),

$$\delta\bar{\mu} = \frac{1}{\Omega} \int_{\text{crystal}} d\vec{r} d\vec{r}' \frac{\delta^2 G[n]}{\delta n(\vec{r}) \delta n(\vec{r}')} \delta n(\vec{r}'). \quad (7)$$

Since our starting point was the uniform-background model, $\delta^2 G/\delta n(\vec{r}) \delta n(\vec{r}')$ must have the form

$$\frac{\delta^2 G[n]}{\delta n(\vec{r}) \delta n(\vec{r}')} = f(\vec{r} - \vec{r}'), \quad (8)$$

where f is, by its definition, a short-range function. Hence

$$\begin{aligned} \delta\bar{\mu} &= \frac{1}{\Omega} \int_{\text{crystal}} d\vec{r} d\vec{r}' f(\vec{r} - \vec{r}') \delta n(\vec{r}') \\ &= \frac{1}{\Omega} \int d\vec{\rho} f(\vec{\rho}) \int_{\text{crystal}} d\vec{r}' \delta n(\vec{r}') = 0, \end{aligned} \quad (9)$$

since the total number of electrons remains constant. This is the desired result.

In Table I, column 2, we reproduce the results for $\Delta\phi_u$, the electrostatic dipole barrier of the uniform-background model, from Ref. 4. Next we use the work-function changes $\delta\Phi$ due to the pseudopotentials, from Ref. 4, together with Eq.

(4) to calculate the corrected dipole barriers $\Delta\phi$, defined by Eq. (2).¹² Here $\bar{\phi}$ is the mean interior electrostatic potential in the pseudopotential model.¹³ These values are listed in columns 4-6.

The dipole barriers $\Delta\phi'$ given in Ref. 7 (the symbol D is used there) were generally considerably smaller than our values of $\Delta\phi_u$ or $\Delta\phi$ (by up to several eV). This was interpreted in Refs. 7-9 as a serious deficiency of the uniform-background model. However, the quantity $\Delta\phi'$ of Ref. 7 does not represent the dipole barrier in the sense of Eq. (2). Rather it is the *additional* barrier, compared with the barrier $\Delta\phi_{ws}$ that exists in a hypothetical reference model in which the half-solid consists of identical perfect Wigner-Seitz cells right up to and including the last layer. To estimate $\Delta\phi_{ws}$, we replace the Wigner-Seitz cells by spheres of radius R , take for the external potential in each cell a potential of the Ashcroft form¹⁴ [these pseudopotentials were used in Ref. 4 to construct $\delta v(\vec{r})$]:

$$v_{\text{pseudo}}(r) = \begin{cases} -Z/r, & r \geq r_c \\ 0, & r < r_c \end{cases}, \quad (10)$$

with r_c determined from bulk properties, and assume the electron density to be uniform in each sphere. In this way we obtain

$$\Delta\phi_{ws} \approx \frac{3}{10} (Z/R) [1 - 5(r_c/R)^2]. \quad (11)$$

In column 7 of the Table we list $\Delta\phi_{ws}$, calculated from (11), and in column 8 the quantity

$$\Delta\phi'' \equiv \Delta\phi_{ws} + \Delta\phi', \quad (12)$$

with $\Delta\phi'$ taken from Ref. 7. This is the quantity

which should be compared with $\Delta\phi_u$ or $\Delta\phi$, and it will be seen that the comparison is rather satisfactory, making allowance for the problem described in the legend of the Table.

We conclude that the same method which we have used in Ref. 4 to calculate work functions also appears to lend itself well to the calculation of surface-dipole barriers of simple metals.

*Supported in part by the Office of Naval Research and the National Science Foundation.

¹J. Bardeen, Phys. Rev. **49**, 653 (1936).

²J. R. Smith, Phys. Rev. **181**, 522 (1969).

³N. D. Lang, Solid State Commun. **7**, 1047 (1969).

⁴N. D. Lang and W. Kohn, Phys. Rev. B **3**, 1215 (1971).

⁵N. D. Lang, in *Solid State Physics*, edited by F. Seitz, D.

Turnbull, and H. Ehrenreich (Academic, New York, 1973), Vol. 28, p. 225.

⁶D. G. Costello, D. E. Groce, D. F. Herring, and J. Wm. McGowan, Phys. Rev. B **5**, 1433 (1972); B. Y. Tong, Phys. Rev. B **5**, 1436 (1972); C. H. Hodges and M. J. Stott, Phys. Rev. B **7**, 73 (1973); P. H. Handel, Z. Phys. **252**, 7 (1972).

⁷V. Heine and C. H. Hodges, J. Phys. C **5**, 225 (1972). We concentrate mainly on this reference in our discussion.

⁸G. Paasch, H. Eschrig, and W. John, Phys. Status Solidi B **51**, 283 (1972). We include here a comment on the method by which the shift of the outermost lattice plane was calculated in this paper. The "lattice" term in the expression for the surface energy in the paper [σ_2 in Eq. (3.8)] may be obtained simply by combining the quantity R defined in Appendix E ("Equilibrium Position of the First Lattice Plane — Effect on Surface Energy") of N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970), with the first term in the expression for the quantity S defined there. All of the other terms in S , however, have been omitted from the treatment of Paasch *et al.*

⁹C. H. Hodges and M. J. Stott, Phys. Rev. B **7**, 73 (1973).

¹⁰P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

¹¹Using Wigner's form of the correlation energy [D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963), Eq. (3.58)], $\bar{\mu}$ for the uniform-background model is given by $\bar{\mu}_u = [3.68r_s^{-2} - 1.22r_s^{-1} - (1.17r_s + 6.9)(r_s + 7.8)^{-2}]$ Ry.

¹²In the case of a finite crystal (whose various faces are of comparable size), $\phi(\infty)$ in Eq. (2) must, of course, be replaced by the electrostatic potential at a point which is outside the central portion of the face of interest and which is a distance away from the face small compared with the face dimensions but large compared with the lattice spacing.

¹³Note that $\bar{\phi}$ is only equal to the often-discussed value $-\frac{2}{3}\epsilon_F$ ($\epsilon_F = \frac{1}{2}k_F^2$, with k_F the Fermi wave vector) if we set $\phi(\infty) = 0$ and if we consider the artificial case of a finite crystal built by superposing, even in the surface region, ions, each of which carries with it the spherically symmetric screening cloud that would surround it if it were alone in a uniform electron gas [i.e., a finite lattice of Ziman's neutral (pseudo-) atoms—see J. M. Ziman, Adv. Phys. **13**, 89 (1964)]. Any relaxation in the surface region away from the electron distribution of this artificial solid would, of course, change $\bar{\phi}$ [assuming $\phi(\infty)$ were held fixed]. These points have also been discussed by C. B. Duke, J. Vac. Sci. Technol. **6**, 152 (1969).

¹⁴N. W. Ashcroft, Phys. Lett. **23**, 48 (1966); N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967); Phys. Rev. **159**, 500 (1967); N. W. Ashcroft, J. Phys. C **1**, 232 (1969)