

Angular terms in the optical potential: Effect on photoemission from a model (100) surface of aluminum

M. Rasolt and H. L. Davis

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 7 May 1979)

Recently derived angular terms in the optical potential are studied in a model calculation for photoemission from the Al(100) surface. The results clearly demonstrate the importance of these contributions, and indicate that they must be included in detailed investigations.

In more recent theoretical studies^{1,2} of electron spectroscopies, and in particular in photoemission analyses, increasing efforts have been made to include detailed features of the electron-electron interaction in describing the propagation of the emitted electron.^{1,2} Such a detailed description is essential for the quantitative interpretation of a vast amount of experimental data on electron-surface interactions, and in discerning the features of the spectra which are surface rather than bulk sensitive. In a recent study, Rasolt and Davis³ have derived additional angular structure in the absorptive part of the electron-electron interaction which is comparable in magnitude to the isotropic terms, highly surface sensitive, and yet totally neglected in any previous description.^{1,2} Here we include such terms in a model photoemission calculation, whose results clearly demonstrate that detailed surface studies should incorporate such contributions.

The detailed analysis producing an angular-dependent optical potential has been presented in Ref. 3, but for completeness we will sketch the key relationships. The interaction of a scattering electron with a surface is described by the Dyson equation⁴

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + v(\vec{r})\right)\phi(\vec{r}, t) + \int d\vec{r}' \Sigma(\vec{r}, \vec{r}', \epsilon_{\vec{p}})\phi(\vec{r}', t) = i\hbar \frac{\partial}{\partial t} \phi(\vec{r}, t), \quad (1)$$

where $\phi(\vec{r}, t)$ is the scattering electron wave func-

tion, $v(\vec{r})$ is the ionic potential screened by the electrostatic field of the electrons, and $\epsilon_{\vec{p}} \equiv p_0 = \hbar^2 p^2 / 2m$. The optical potential can be written:

$$\Sigma(\vec{r}, \vec{r}', \epsilon_{\vec{p}}) = V_r(\vec{r}, \vec{r}', \epsilon_{\vec{p}}) + iV_i(\vec{r}, \vec{r}', \epsilon_{\vec{p}}). \quad (2)$$

Of particular interest is the structure of the imaginary part, which is second in importance only to the ion potential in describing the details of the above processes.

In practice $V_i(\vec{r}, \vec{r}', \epsilon_{\vec{p}})$ is usually considered to be independent of position and of the direction of the electron beam.⁵ This is clearly a severe approximation in the surface region.⁶ Neglected in such an approximation are terms that depend on the direction of \vec{p} relative to the surface normal \hat{z} . Such dependence is a consequence of the broken symmetry along the z axis introduced by the surface. Following Sham and Kohn,⁷ the isotropic V_i is written as

$$iV_i(\vec{r}, \vec{r}', p_0) = iV_i^h(\vec{r} - \vec{r}', p_0 - v(\vec{r}), n(\vec{r})) + iV_i^h(\vec{r}' - \vec{r}, p_0 - v(\vec{r}'), n(\vec{r}')). \quad (3)$$

The $v(\vec{r})$ in Eq. (3) will be neglected since in this work $p_0 \gg |v(\vec{r})|$. The approximation of Eq. (3) will clearly be the leading term of a gradient expansion⁷ of a system of slowly varying density. The hope is that it will remain adequate for actual electronic systems in which the density sometimes varies rather rapidly.

We now generalize Eq. (3) to include higher-order terms in the gradient expansion for V_i ,

$$iV_i(\vec{r}, \vec{r}', p_0) \approx iV_i^h(\vec{r} - \vec{r}', p_0, n(\vec{r})) + i[\nabla n(\vec{r}) \cdot \nabla g_1(\vec{r} - \vec{r}', p_0, n(\vec{r})) + \nabla' n(\vec{r}') \cdot \nabla' g_1(\vec{r}' - \vec{r}, p_0, n(\vec{r}))] + \frac{1}{8}i\{\nabla^2 \nabla^2 [n(\vec{r})g_2(\vec{r} - \vec{r}', p_0, n(\vec{r}))] + \nabla'^2 \nabla'^2 [n(\vec{r}')g_2(\vec{r}' - \vec{r}, p_0, n(\vec{r}'))]\} + O(\nabla n \cdot \nabla n). \quad (4)$$

There are other terms we can introduce into the non-Hermitian structure of Eq. (4), but the above form is sufficient and consistent within our order of approximation. If we now apply a WKB-type approximation⁷ (i.e., $\phi(\vec{r}) \approx e^{i\vec{p}(\vec{r}) \cdot \vec{r}}$) in Eq. (1), we obtain from Eq. (4)

$$i \int d\vec{r}' V_i(\vec{r}, \vec{r}', p_0)\phi(\vec{r}', t) = i[V_i^h(\vec{p}(\vec{r}), p_0, n(\vec{r})) - g_2(\vec{p}(\vec{r}), p_0, n(\vec{r}))(\vec{p} \cdot \nabla)(\vec{p} \cdot \nabla)n(\vec{r}) + O(\vec{p} \cdot \nabla n \vec{p} \cdot \nabla n)]\phi(\vec{r}, t). \quad (5)$$

Of course, a full exposition of all the terms of Eq. (4) in Eq. (5) would reveal additional contributions proportional to $i|\vec{p}(\vec{r})|^2$. However, these terms depend only on the magnitude of the momentum \vec{p} and will therefore not add any anisotropic features to $iV_i^h(\vec{p}, p_0, n(\vec{r}))$. Such contributions can be viewed as being part of $iV_i^h(|\vec{p}|)$, which is obtained on averaging the first term in Eq. (5) over \vec{r} . To order $\nabla^2 n$ only the last two terms in Eq. (4) introduce intrinsic angular dependence on \vec{p} in Σ .

To make a connection between g_2 of Eq. (5) and the electron gas vertex function $\Lambda(\vec{p} + \vec{q}, \vec{p}, p_0, n_0)$ is not difficult and we write only the final result below. If we expand

$$\begin{aligned} \tilde{\Lambda}(\vec{p} + \vec{q}, \vec{p}, p_0, n_0) \\ \approx -1 + \tilde{\Lambda}(\vec{p}, \vec{p}, p_0, n_0) + \tilde{\Lambda}'(\vec{p}, \vec{p}, p_0, n_0) \vec{p} \cdot \vec{q} \\ + \tilde{\Lambda}''_a(\vec{p}, \vec{p}, p_0, n_0) (\vec{p} \cdot \vec{q})^2 \\ + \tilde{\Lambda}''_b(\vec{p}, \vec{p}, p_0, n_0) q^2, \end{aligned} \quad (6)$$

then

$$g_2(\vec{p}, p_0, n_0) = -\text{Im} \frac{\tilde{\Lambda}''_a(\vec{p}, \vec{p}, p_0, n_0)}{\pi(0)}, \quad (7)$$

where $\pi(0) \equiv \lim_{q \rightarrow 0} \pi(q)$ of the static screening function. The $\nabla n \cdot \nabla n$ contribution is neglected, since

$$\begin{aligned} \text{Im} \Lambda''_a(\vec{p}, \vec{p}, p_0, n_0) = \frac{-e^2 m^2 \omega_p}{12 p^4 \gamma(p, n_0)} \Theta^> \left(\frac{p^2}{2m} - \frac{k_F^2}{2m} - \omega_p \right) \Theta^< (k_c - p + \gamma(p, n_0)) \\ \times \left[\left(\frac{3}{p[p - \gamma(p, n_0)]} + \frac{3}{[p - \gamma(p, n_0)]^2} + \frac{2p}{[p - \gamma(p, n_0)]^3} \right) \right. \\ \left. - \left(\frac{3}{p[p + \gamma(p, n_0)]} + \frac{3}{[p + \gamma(p, n_0)]^2} + \frac{2p}{[p + \gamma(p, n_0)]^3} \right) \right], \end{aligned} \quad (8)$$

where $\gamma(p, n_0) = (p^2 - 2m\omega_p)^{1/2}$ and $\Theta^>(x) = 1$ for $x > 0$ and 0 for $x < 0$. For application to aluminum we choose for $n(\vec{r})$ the Lang-Kohn⁶ density of a step jellium surface with bulk density $r_s = 2$. The anisotropic contribution to Σ is then given by

$$\begin{aligned} -g_2(\vec{p}, p_0, n(\vec{r})) (\vec{p} \cdot \nabla) (\vec{p} \cdot \nabla) n(\vec{r}) \\ = \text{Im} \Lambda''_a(\vec{p}, \vec{p}, p_0, n(z)) \frac{(\vec{p} \cdot \hat{z})^2}{\pi(0)} \frac{\partial^2 n(z)}{\partial z^2}, \end{aligned} \quad (9)$$

with $\pi(0) = m k_F / \hbar^2 \pi^2$.¹⁰ Equations (8) and (9) represent the anisotropic contributions to the optical potential within the RPA. Since Eq. (9) contains $\partial^2 n / \partial z^2$, these anisotropic contributions will be highly sensitive to density variations in the surface region.

Equation (9) has been evaluated for Al and the results are displayed in Fig. 1. To investigate possible influences on photoemission, we performed calculations for a model corresponding to

it represents second-order scattering, and is expected to be small for large momentum p .

Equation (7) has been evaluated within the RPA,³ and the approach is only summarized below. First, the contributions from two-plasmon processes are neglected. These are higher-order corrections and hence not likely to change our estimates and conclusions concerning the order of magnitude of the anisotropic terms, which is the purpose of the work. Second, the anisotropic contributions are estimated as follows. $\epsilon(k, k_0)$ is the dynamically screened interaction for the homogeneous electron gas. It is known to misrepresent the interaction at a metal surface for small wave-vector fluctuations.⁸ A cutoff k_c (chosen here from Ref. 9 as $k_c = 0.123 k_{\text{Thomas-Fermi}}$) is introduced to reflect this. For $k > k_c$ we approximate $\epsilon(k, k_0)$ by the single-plasmon pole approximation, $\epsilon(k, k_0) \approx 1 - \omega_p^2 / (k_0 + i\delta)^2$. For $k < k_c$ surface plasmons are important and another form for $\epsilon(k, k_0)$ was chosen from Ref. 8. These surface-plasmon contributions were then evaluated and found to make only small corrections to the scattering amplitude $\phi(\vec{r}, t)$.

To estimate the anisotropic contributions to V_i , our final result for $\text{Im} \Lambda''_a$ in Eqs. (6) and (7) then is

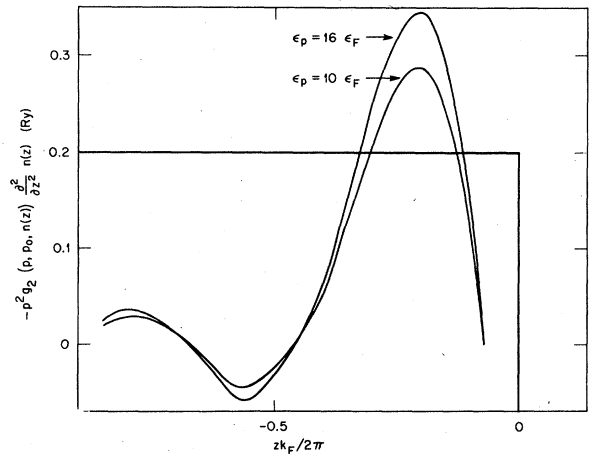


FIG. 1. The anisotropic contribution to the optical potential [Eq. (9)] as a function of position z for two different energies of the scattering electron. The step jellium background is also shown.

the Al(100) surface,¹¹ where we denote the perpendicular spacing between layers as d . Equation (9) implies that the optical potential is of the form

$$\Sigma = V_r + i[\epsilon_2(z) + \epsilon_3(z) \cos^2 \theta_p], \quad (10)$$

where θ_p is the angle between \vec{p} and \hat{z} . Using the position of the atomic layer relative to the jellium density of Al as specified in Ref. 6, we approximate¹² the z dependence of Eq. (10) as follows. We set $\epsilon_2(z) = -6$ eV and $\epsilon_3 = +2$ eV for z in the region from $d/4$ on the vacuum side to $d/2$ on the material side of the first atomic layer, and $\epsilon_2(z) = -4$ eV and $\epsilon_3 = 0$ elsewhere.¹³

In the calculations performed, the electron emission was assumed to occur in either the first or second atomic layer. Since our interest was in the influence of V_i on the final state and not in the details of the emission process, electron emission at an atomic site was represented by a single partial wave of the form

$$\kappa^{1/2} B_{lm} h_l^{(1)}(\kappa |\vec{r} - \vec{r}_n|) Y_{lm}(\vec{r} - \vec{r}_n). \quad (11)$$

Some results for $E = 60$ eV are presented in Fig. 2, which also contains results for an isotropic V_i defined by $\epsilon_2 = -4$ eV and $\epsilon_3 = 0$ throughout the entire surface region.

The results of Fig. 2 clearly demonstrate that there are noticeable effects of anisotropies in V_i , and that such effects should be considered in any detailed studies of photoemission processes.^{1,2} It is seen that the effects are more pronounced when emission occurs in the first atomic layer, which reflects the sensitivity of Eq. (9) to the density variations in the immediate surface region. Also, it is noted that higher-angular-momentum states [e.g., (2,2)] show a larger effect, which is a consequence of the angular dependence in emission coupling with the angular dependence in the anisotropic optical potential. Clearly the results of Fig. 2 are for a simple model. But since noticeable effects are evident in these results, future

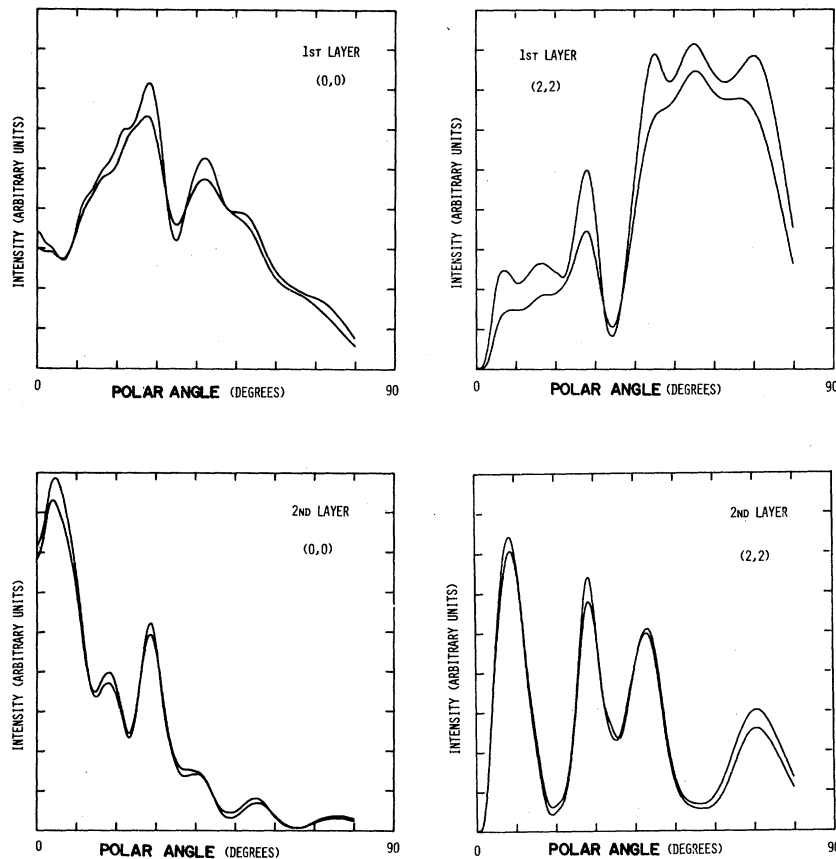


FIG. 2. Results from model photoemission calculations for an Al(100) surface. The upper curve and lower curve in each subplot were obtained using, respectively, an isotropic and anisotropic imaginary part of the optical potential. The azimuthal angle for the calculations coincided with a $\langle 011 \rangle$ direction. In each subplot the layer where the emission occurred and the angular momentum (l, m) of the emitted wave are indicated.

studies will examine in greater detail the explicit dependence of Eq. (9) on density variations.

We wish to acknowledge Dr. Mark Mostoller for critical comments concerning this manuscript.

The research for this work was sponsored by the Division of Materials Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

¹D. R. Penn, Phys. Rev. Lett. 38, 1429 (1977).

²R. J. Baird, C. S. Fadley, S. M. Goldberg, P. J. Feibelman, and M. Sunjic, Surf. Sci. 72, 495 (1978).

³M. Rasolt and H. L. Davis, Phys. Rev. B 20, 5059 (1979).

⁴L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.

⁵J. E. Demuth, P. M. Marcus, and D. W. Jepsen, Phys. Rev. B 11, 1460 (1975).

⁶N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

⁷L. J. Sham and W. Kohn, Phys. Rev. 145, 561 (1966).

⁸D. C. Langreth and J. P. Perdew, Phys. Rev. B 15, 2884 (1977).

⁹V. Peuckert, J. Phys. C 9, 4173 (1976).

¹⁰See, for example, J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1964).

¹¹D. W. Jepsen, P. M. Marcus, and F. Jona, Phys. Rev. B 5, 3933 (1972).

¹²In future applications we will employ the actual density variation. For an initial calculation, the approximation used herein is sufficient to demonstrate the importance of the anisotropy.

¹³For $\theta_p = 0$, this specification gives $\epsilon_2 + \epsilon_3 = -4$ eV, which is the isotropic value used in Ref. 11.