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A One-Step Model of Photoemission from Single Crystal Surfaces

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In this paper, we present a 3-D one step photoemission model that can be used to calculate the quantum efficiency and momentum distributions of electrons photoemitterd from ordered single crystal surfaces close to the photoemission threshold. Using Ag(111) as an example, we show that the model can not only calculate the quantum efficiency from the surface state accurately without using any ad hoc parameters, but also provides a theoretical quantitative explanation of the vectorial photoelectric effect. This model in conjunction with other band structure and wave function calculation techniques can be effectively used to screen single crystal photoemitters for use as electron sources for particle accelerator and ultrafast electron diffraction applications.

I. INTRODUCTION

Over the past few decades photoemission based tools like Photoelectron Spectroscopy (PES) and Angle-Resolved Photoelectron Spectroscopy (ARPES) have proven extremely successful in studying the chemical and electronic structure of solid state materials and surfaces.\(^1\) As a result, physics of the photoemission phenomena has been well investigated with regards to explaining the angle resolved electron energy spectra obtained using UV and X-ray light sources.

More recently, photoemission has gained popularity as a source of electrons for several applications like Free Electron Lasers (FELs)\(^2\) and Ultrafast Electron Diffraction (UED)\(^3\) experiments. The quantum efficiency (QE) and the transverse (to the normal on the photoemission surface) momentum spread or the rms transverse momentum are the most critical figures of merit of the photoemission based electron sources (or photocathodes) that limit the performance of such applications.\(^4\) For example, the transverse coherence length of the electron beam in UED which limits the largest lattice size that can be studied is inversely proportional to the rms transverse momentum of electrons emitted from the cathode.\(^5\) The transverse momentum spread also limits the smallest possible rms transverse momentum through ultrafast laser heating of the electron gas.\(^6\) Hence a high QE is required.

Despite the technological importance of solid state photoemission as an electron source, the physics that governs the relevant photoemission properties of QE and rms transverse momentum is not well understood. The first theory to model these photoemission parameters from metal cathodes was proposed by Dowell and Schmerge and followed a three step photoemission model\(^7\). This theory successfully explained the QE and rms transverse momentum obtained from polycrystalline or disordered cathodes but did not model photoemission very close to the threshold accurately. An extension to this theory was developed recently, to model photoemission near the threshold.\(^8\) It showed that the smallest possible rms transverse momentum from polycrystalline surfaces is thermally limited by the temperature of the lattice. However these models did not include the effects of band structure, polarization and angle of incident light (the vectorial photoelectric effect)\(^9\) and did not model emission from single crystal surfaces of metals. A technique to estimate the rms transverse momentum spread from single crystal faces of metal cathodes using the band structure calculated from density functional theory was developed by Schroeder et al.\(^10\) However, this technique does not estimate the QE and assumes uniform probability of photoemission from any given electron state which is generally not true.

In this paper, we present a scheme to calculate the QE and transverse momentum spread accurately using an one-step photoemission model. Our model is a 3-D expansion of the 1-D photoemission model developed by Miller et al.\(^11\) to explain ultraviolet photoemission spectra (UPS) obtained from single crystals surfaces of noble metals. Photoemission is modelled as a one step process of the transition of electrons from the initial bulk or surface state (ss) inside the metal to a time-reversed LEED like free electron state under the influence of the electromagnetic field of the incident light. We obtain the rate of such a transition using the Fermi golden rule to calculate the QE and the rms transverse momentum of
emitted electrons. This photoemission model takes into account the effects of band structure, polarization and angle of incident light.

Using the (111) surface of silver as an example, we show that our model predicts the QE near threshold accurately and explains the effects of polarization of incident light and angle of incidence quantitatively. We show that the emission from an Ag(111) surface at threshold, at an angle of incidence near 60° is dominated by the electrons emitted from the Shockley surface state$^{10}$ resulting in a QE of greater than $5 \times 10^{-5}$ very close to the photoemission threshold. We also calculate the rms transverse momentum of electrons emitted from the Ag(111) surface. We show that the Ag(111) surface can simultaneously provide a high QE and a low rms transverse momentum of electrons emitted from the Ag(111) surface.

The dependence of QE on the polarization of incident light and angle of incidence is called the vectorial photoelectric effect and has been investigated experimentally, but has been modeled only empirically$^{11,12}$. Using our scheme to calculate the QE we show that the vectorial photoelectric effect results from the variation of the overlap integral with the angle of incidence and polarization of incident light and can be modeled without use of any empirical data.

II. THE ONE-STEP MODEL

A. Basic Formalism

We assume that the normal to the solid-vacuum interface is along the z direction and the classical interface is located at $z = 0$, with $z > 0$ being the vacuum side. The Hamiltonian of the photon-electron interaction is given by

$$\mathcal{H} = \frac{1}{2m_e} \left( \frac{\vec{p} - e \vec{A}}{c} \right)^2 - \frac{p^2}{2m_e} \approx -\frac{\hbar e}{m_e c} \vec{A} \cdot \vec{\nabla} \left( \vec{\nabla} \cdot \vec{A} \right)$$

where $\vec{p}$ is the momentum operator, $\vec{A}$ is the vector potential of the incident light, $e$ is the unit charge, $c$ is the speed of light and $m_e$ is the mass of a free electron in vacuum.

The vector potential of incident light inside the metal surface can be given by $\vec{A} = A_0 e^{\frac{z - z_0}{d_0}} \vec{\epsilon}$, where $A_0$ is the magnitude of the vector incident potential just outside the surface, $\vec{\epsilon}$ is the polarization vector inside the surface, $d_0$ is the decay length of the incident light in the metal and $z_0$ is the location of the interface adjusted to account for the spilling over of the electron cloud into vacuum$^{11,12}$ due to the surface state. For the Ag(111) surface $z_0$ is determined by wave function matching of the Shockley surface state at the solid-vacuum interface as shown in section III B. Note that the magnitude of polarization vector $\vec{\epsilon}$ is not unity and takes into account the reflection at the surface as given in section II B. The incident photon flux per unit area is given by

$$F = \frac{2\varepsilon_0 |A_0|^2}{\hbar c} \frac{\omega}{\cos (\theta_i)} \cos (\theta_i)$$

where $\omega$ is the frequency of incident light, $\varepsilon_0$ is the dielectric constant of vacuum and $\theta_i$ is the angle of incidence,$^{17}$.

For ultra-violet light, the wavelength is long enough that the $\vec{\nabla} \cdot \vec{A}$ term in equation 2 can be ignored everywhere except at the metal-vacuum interface. At the metal-vacuum interface, there is a sharp discontinuity in $\vec{A}$ in the z direction and $\vec{\nabla} \cdot \vec{A}$ results in a delta function at $z = z_0$. The Hamiltonian is then given by

$$\mathcal{H} = -\frac{\hbar eA_0}{m_e c} \left( \vec{\epsilon} \cdot \vec{\nabla} + C \varepsilon_0 \delta (z') \right)$$

where $\varepsilon_z$ is the $z$ component of $\vec{\epsilon}$, $H (z)$ is the Heaviside function, $z' = z - z_0$ and $C$ is a constant that depends only on the photon energy and the properties of the solid. The constant $C$ can be obtained by fitting the calculations of the 1D model to the photoemission electron spectroscopy data.$^{13,15}$

Photoemission from single crystal surfaces can be modeled as a transition process of an electron between an initial bulk or surface state (ss) inside the lattice with wave function $\phi_i$ to a time reversed LEED like free electron state in vacuum with wave function $\phi_f$ under the influence of incident light$^{11,12}$. The total transition rate of this process is given by Fermi’s golden rule as

$$R = \sum_i \sum_f \frac{4\pi}{\hbar} |\langle \phi_f | H | \phi_i \rangle|^2 \delta (E_f - (E_i + \hbar \omega)) F (E_i)$$

where the summations are over all possible initial and final states, $E_i$ and $E_f$ are the energies of the initial and final states respectively, the $\delta$ function enforces the conservation of energy and $F (E_i) = \left(1 + \exp \left(\frac{E_i}{k_B T}\right) \right)^{-1}$ is the Fermi-Dirac distribution. $k_B$ is the Boltzmann constant and $T$ is the temperature of the lattice. Note that we have assumed the Fermi level to be 0. The expression for the transition rate includes a factor of 2 to account for the two possible electron spins.

We work within the box approximation to assume that the volume under consideration extends from $-L/2$ to $L/2$ in all directions and $L \rightarrow \infty$. Within this assumption we can convert the summations in equation 5 to integrals and rewrite the transition rate as

$$R = \frac{4\pi}{\hbar} \left( \frac{L}{2\pi} \right)^6 \int d\vec{k}_i \int d\vec{k} M^2 \delta (E_f - (E_i + \hbar \omega)) F (E_i)$$

where $M = |\langle \phi_f | H | \phi_i \rangle|$ is the overlap integral or the matrix element. $\vec{k}_i = k_{ix} \hat{x} + k_{iy} \hat{y} + k_{iz} \hat{z}$ is the wave vector of electrons in their initial state and $\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}$
is the wave vector of the emitted electron. If the work function of the emission surface is \(W\), the energy of the final state, \(E_f\), can be written as

\[
E_f = \frac{\hbar^2 k^2}{2 m_e} + \frac{\hbar^2 k^2}{2 m_e} + W,
\]

where \(k = \sqrt{k_x^2 + k_y^2}\) is the wave number of the emitted electron in the transverse direction \((x-y)\) plane. The delta function in equation 6 can then be written as

\[
\delta(E_f - (E_i + \hbar \omega)) = \frac{\sqrt{m_e}}{\hbar \sqrt{2X}} \delta(k_z - k_{z0})
\]

where \(k_{z0} = \sqrt{2 m_p X}\), \(X = E_i + \hbar \omega - \frac{\hbar^2 k^2}{2 m_e} - W\).

The QE can simply be calculated as

\[
\text{QE} = \frac{R}{F L^2}
\]

As will be shown in the following section, the QE is independent of \(L\) as the matrix element is proportional to \(1/L^2\) owing to the normalization of the wave functions within the bounding box.

The transverse momentum spread or the rms transverse momentum can be calculated as

\[
\langle p_{z}^2 \rangle = \left[ \frac{\int d^3 k_i \int d^3 k_f \hbar^2 k_i^2 M^2 \delta(E_f - (E_i + \hbar \omega)) F(E_i) \int d^3 k_i \int d^3 k_f M^2 \delta(E_f - (E_i + \hbar \omega)) F(E_i)}{\int d^3 k_i \int d^3 k_f \hbar^2 k_i^2 M \delta(E_f - (E_i + \hbar \omega)) F(E_i) \int d^3 k_i \int d^3 k_f \hbar^2 k_i^2 M \delta(E_f - (E_i + \hbar \omega)) F(E_i)} \right]^{\frac{1}{2}}
\]

One can obtain the QE and the rms transverse momentum by calculating the matrix elements \(M\) and evaluating the integrals in equation 6. Calculation of the matrix elements cannot be generalized further and requires the knowledge of the band structure, wave functions and the orientation of the photo-emitting surface. In the next section, we calculate the matrix elements and perform the integrals to obtain the QE and the rms transverse momentum for the \(Ag(111)\) surface as an example.

### B. Refraction of Light at the Solid-Vacuum Interface

In order to calculate the matrix elements, one needs to obtain the polarization vector \(\hat{c}\) for incident light inside the solid surface. Expressions to obtain \(\hat{c}\) can be found in Born and Wolf’s Principles of Optics[19] or any other standard text on electromagnetic waves. However, we state them here for the sake of completion.

We assume \(x-z\) plane to be the plane of incidence. The complex angle of transmission is given by Snell’s law as

\[
\theta_t = \arcsin \left( \frac{1}{n} \sin \theta_i \right)
\]

where \(n = n_r + i n_i\) is the complex index of refraction, \(\theta_i\) is the angle of incidence.

The angle of the light wave vector inside the metal with respect to the \(z\) axis can be given by

\[
\theta_t = \arctan \left[ \frac{\sin \theta_i}{q \left( n_r \cos \gamma - n_i \sin \gamma \right)} \right]
\]

and the optical decay length for the fields can be given by

\[
d_i = \frac{c}{\omega q \left( n_i \cos \gamma + n_r \sin \gamma \right)}.
\]

For \(p\)-polarized light the polarization vector of the vector potential is

\[
\hat{c} = T_p \sin \theta_i \hat{z} + T_p \cos \theta_i \hat{x},
\]

where

\[
T_p = \frac{2 \cos \theta_i}{\cos \theta_i + n \cos \theta_i}.
\]

For \(s\)-polarized light the polarization vector of the vector potential is

\[
\hat{c} = T_s \hat{y},
\]

where

\[
T_s = \frac{2 \cos \theta_i}{n \cos \theta_i + \cos \theta_i}.
\]

### III. PHOTOEMISSION FROM Ag(111)

In this section, we demonstrate the use of the formalism developed above to obtain analytic expressions for the QE and rms transverse momentum from a Ag(111) surface. The calculated QE matches the experimental values showing the effectiveness of the formalism developed above.

#### A. Band structure of Ag(111)

We use a two-band fit to the nearly free-electron like Ag \(sp\) band dispersion model around the \(L\) point[20]. The total energy \((E_{i,f})\) can be divided into the longitudinal part \((E_{zi,zf})\) and the transverse part \((E_{ri,rf})\) and can be written as

\[
E_{i,f} = E_{zi,zf} + E_{ri,rf}
\]
Longitudinal effective mass parameter of the lower sp band at the zone boundary, \( p \), pseudo potential form factor and equals one-half of the valance band maximum, \( V \), at the lower and upper sp bands respectively, \( L \) vector at the point and is equal to \( 100 \) meV. The Fermi level is assumed to be 0. The scale for \( k_{z,i,zf} \) is chosen such that the zero lies at the \( L \) point.

The dispersion relation in the transverse directions (\( x-y \) plane) is assumed to be cylindrically symmetric and can be modeled by nearly parabolic bands given by

\[
E_{ri,rf} = \frac{\hbar^2 k_{ri,rf}^2}{2m_{ri,rf}} + \sum_{n=3}^{6} \eta_{ni,rf} k_{ri,rf}^n
\]

where \( E_{ri,rf} \) are the transverse energies of the electrons in the lower and upper sp bands respectively, \( k_{ri,rf}^2 = k_{x,i,zf}^2 + k_{y,i,zf}^2 \) and \( m_{ri,rf} \) are the transverse effective masses of the lower and upper sp bands respectively. The coefficients \( \eta_{ni,rf} \) are higher order correction coefficient obtained by fitting the band structure of silver.

Figure 1 shows the band structure of Ag projected along the [111] direction. The pink shaded region is the lower sp bands filled with electrons. The states of this band that extend beyond the Fermi level are unoccupied and not shown. The region shaded in blue is the upper sp band which is unoccupied. The solid blue curves are contours of constant \( E_{zi,zf} \) or correspondingly constant \( k_{zi,zf} \). The green curve is the ‘free electron parabola’ corresponding to a photon energy of \( \hbar \omega \). The conservation of energy and transverse momentum allow only the occupied states above this parabola to be emitted.

### 1. Band structure of bulk states

Within the framework of the nearly free electron model, the dispersion relations for the two bands in the longitudinal direction (111 or \( z \) direction) are given by

\[
E_{zi,zf} = E_v + V + \frac{\hbar^2 k_{zi,zf}^2}{2m_{i,f}} + \left( \frac{\hbar^4 p^2 k_{zi,zf}^2}{2m_{i,f}^2} + V^2 \right)^{1/2}
\]

where \( E_{zi,zf} \) are the longitudinal energies of the electrons in the lower and upper sp bands respectively, \( E_v \) is the valance band maximum, \( V \) is the absolute value of the pseudo potential form factor and equals one-half of the gap at the zone boundary, \( p \) is the magnitude of the wave vector at \( L \) point and is equal to \( \sqrt{\frac{4\pi}{a}} \) (\( a \) being the lattice constant) and \( m_{i,f} \) are the effective mass parameters of the lower and upper sp bands respectively. It should be noted that \( m_{i,f} \) represent higher order corrections from multi band effects and do no correspond to the curvature of the dispersion relations. The subscripts \( i \) and \( f \) represent the lower and upper sp bands respectively.

\( \eta \) is the absolute value of the wave vector at \( \mathbf{F} \) point with energy \( E_{\mathbf{F}} \) and \( \eta \) is imaginary for the surface state.\(^{22}\) The shape of these contours is nearly parabolic and given by equation \( 22 \) with an offset of \( E_{zi,zf} \).

Values of all parameters used for modeling the bulk band structure are given in table 1 and were obtained by fitting the band structure of silver.

### 2. Band structure of surface state

Ag(111) exhibits a Shockley surface state\(^{14}\) within the band gap at the \( L \) point with energy \( E_s \). The surface state has \( E_{zi} = E_s \). Since the surface state is located within the band gap, \( k_z \) obtained from equation \( 21 \) is imaginary for the surface state.\(^{22}\) The dispersion relation in the transverse direction is parabolic and given by

\[
E_{ri} = \frac{\hbar^2 k_{ri}^2}{2m_s}
\]

The effective mass of the surface state has been measured to be \( m_s = 0.40m_e \).\(^{23}\) The energy of the surface state \( E_s \) can change significantly with the sample and surface preparation methods and is sensitive to the strain in the crystal. At room temperature it has been reported to range between -20 meV to -120 meV.\(^{23,24}\) Here, we use it as a fitting parameter and obtain the best fit for QE at \( E_s = -100 \) meV.

| Symbol | Description | Value |
|--------|-------------|-------|
| \( m_s \) | Longitudinal effective mass parameter of the lower sp band | \( 0.80m_e \) |
\begin{table}[h]
\begin{tabular}{|c|c|}
\hline
$m_f$ & Longitudinal effective mass parameter of the upper $sp$ band 0.90$m_e$  \\
$m_{e1}$ & Transverse effective mass of lower $sp$ band 0.35$m_e$  \\
$m_{e1}$ & Transverse effective mass of upper $sp$ band 2.60$m_e$  \\
$m_s$ & Effective mass of surface state 0.40$m_e$  \\
$\eta_{3i}$ & Third order correction coefficient for lower $sp$ band $-0.8 \times 10^{-5}$ eVnm$^2$  \\
$\eta_{4i}$ & Fourth order correction coefficient for lower $sp$ band $-1.0 \times 10^{-5}$ eVnm$^2$  \\
$\eta_{5i}$ & Fifth order correction coefficient for lower $sp$ band $-3.5 \times 10^{-5}$ eVnm$^2$  \\
$\eta_{6i}$ & Sixth order correction coefficient for lower $sp$ band $12.5 \times 10^{-6}$ eVnm$^2$  \\
$\eta_{3f}$ & Third order correction coefficient for upper $sp$ band $2.2 \times 10^{-5}$ eVnm$^2$  \\
$\eta_{4f}$ & Fourth order correction coefficient for upper $sp$ band $-6.5 \times 10^{-5}$ eVnm$^2$  \\
$\eta_{5f}$ & Fifth order correction coefficient for upper $sp$ band $-5.6 \times 10^{-5}$ eVnm$^2$  \\
$\eta_{6f}$ & Sixth order correction coefficient for upper $sp$ band $20.8 \times 10^{-6}$ eVnm$^2$  \\
$E_s$ & Energy of surface state $-100$ meV  \\
$E_{xc}$ & Valence band maximum at L point $-178$ meV  \\
$V$ & Pseudo potential form factor (equals one half band gap at L point) 2.1 eV  \\
$W$ & Work function of Ag(111) 4.45 eV  \\
$a$ & Unit cell length 0.409 nm  \\
\hline
\end{tabular}
\caption{List of symbols and values used to model the band structure of Ag(111) surface}
\end{table}

B. Wave functions

Close to the $L$ point, the $x$ and $y$ dependent part of the initial and final wave functions can be expressed as plane waves. Thus the initial and final wave functions can be expanded as $\phi_i = \phi_{zi} e^{i(k_{zi} x)} e^{i k_{zi} y}$ and $\phi_f = \phi_{zf} e^{i k_{zf} x} e^{i k_{zf} y}$ respectively. In order to match the transverse part of the final wave functions at the boundary we require $k_{zf} = k_x$ and $k_{zf} = k_y$. Below we give the $z$ dependent parts of the wave functions.

1. Initial Bulk States

The $z$ dependent part of the initial wave functions for the bulk states inside the Ag(111) surface can be given by the combination of two Bloch states ($k_{zi} + p$ and $k_{zi} - p$) of the lower $sp$ band and outside the surface can be given by an exponential decay. Thus for $z < z_0$

$$\phi_{zi} = N \left\{ e^{i(k_{zi} + p) z} + \psi_i e^{i(k_{zi} - p) z} + c_1 e^{-i(k_{zi} + p) z} + \psi_i e^{-i(k_{zi} - p) z} \right\}$$  \hspace{1cm} (24)

and for $z \geq z_0$

$$\phi_{zi} = N c_2 e^{-\kappa_{zi} z'}$$  \hspace{1cm} (25)

where $\kappa_i = \sqrt{2 m_e (W - E_{zi})}/h$.

The normalization constant $N$ can be obtained by normalizing the wave function. Constants $c_1$ and $c_2$ are obtained by matching the wave function and its derivative at $z = z_0$. The expressions for $\psi_i$, $N$, $c_1$ and $c_2$ are given in the appendix.

2. Initial Surface States

For the surface state $E_{zi} = E_s$, $k_{zi} = k_{zs}$, $\phi_{zi} = \phi_{zs}$ and $\psi_i = \psi_s$. The energy of the surface state ($E_s$) lies withing the $L$ gap. Hence, from equation (21) we see that the value of $k_{zs}$ is imaginary causing the surface state to decay into the bulk.

For $z < z_0$ the wave function of the surface state (ss) is given by

$$\phi_{zs} = N_s \left[ e^{i(k_{zs} + p) z} + \psi_s e^{i(k_{zs} - p) z} \right]$$  \hspace{1cm} (26)

and for $z > z_0$ it is given by

$$\phi_{zs} = N_s c_s e^{-\kappa_{zs} z'}$$  \hspace{1cm} (27)

where $\kappa_s = \sqrt{2 m_e (W - E_s)}/h$. $N_s$ is the normalization constant and can be obtained by normalizing the wave function. $c_s$ and $z_0$ can be obtained by matching the wave function and its derivative at $z = z_0$. Expressions for $N_s$ and $c_s$ are given in the appendix. An explicit expression cannot be obtained for $z_0$ and its value needs to be calculated numerically to satisfy the continuity conditions of the wave functions as given in the appendix.

3. Final States

The final state wave functions are not the free electron wave functions of the emitted electron, but are time reversed LEED states as required by the one step photomission theory. Inside the Ag(111) surface they can be given by the combination of two Bloch states ($k_{zi} + p$ and $k_{zi} - p$) of the upper $sp$ band along with an exponential decay to account for the various scattering mechanisms that prevent emission of excited electrons. The final wave functions outside the surface are plane waves. Thus for $z < z_0$
\( \phi_{zf}^* = t_{pk}^* e^{i(k_zz_f + p_d)z} + \psi_f e^{i(k_zf - p_d)z} \sqrt{\frac{2}{L}} \)

where \( k_d = s/d_{e-e} \) is the exponential decay constant that takes into account the scattering mechanisms that prevent emission of excited electrons. \( d_{e-e} \) is the electron-electron scattering length, which is the dominant scattering mechanism in metals. The scattering parameter \( s \) is used as a fitting parameter in the calculation.

For \( z \geq z_0 \)

\( \phi_{zf}^* = \left[ e^{-ik_zz'} + r_{pk}^* e^{ik_zz'} \right] \sqrt{\frac{2}{L}} \quad (29) \)

where \( h k_z = \sqrt{2m_e (E_{fz} - W)} \) is the momentum of the emitted electron in the \( z \) direction. Constants \( t_{pk}^* \) and \( r_{pk}^* \) are obtained by matching the wave functions and their derivative at \( z = z_0 \). Expressions for \( \psi_f, t_{pk}^* \) and \( r_{pk}^* \) are given in the appendix. Note that the normalization of the final states is such that the outgoing plane wave representing the emitted photoelectron is normalized to unity.

Figure 2 shows an example of the real component of the \( z \) dependent part of the initial bulk (a), surface (b) and final (c) wave functions. Here \( z_0 = 0.042 \) nm and \( s = 12.5 \).

Using the wave functions given in the previous section and integrating over the box one can calculate \( M^2 \) for \( p \) polarized light as

\[
M^2 = \frac{4K_1 |T_p|^2}{L^4} k_z^2 \left| (I_d + CI_s) \sin \theta_t + ik_{xi}I \cos \theta_t \right|^2 \\
\times \ h (k_{z i} - k_{xf}) h (k_{yi} - k_{yf})
\]

where \( K_1 = e^2 \hbar^2 |A_{0i}|^2 \) and \( h (\zeta) = \frac{1}{L} \left[ \frac{2 \sin (L\zeta/2)}{L\zeta} \right]^2 \). Note that in the limit \( L \to \infty \), \( h (\zeta) = \frac{2}{L} [\sin (L\zeta/2)]^2 \) and \( I_d, I_s \) and \( I \) are given as follows

\[
I_d = \frac{L^2}{2} \int_{-L/2}^{L/2} dz \phi_{fz}^* e^{-i\mu(z')} \left\{ \frac{\partial}{\partial z} \phi_{zi} \right\} \\
I_s = \frac{L^2}{2} \phi_{fz}^* (z_0) \phi_{zi} (z_0) \\
I = \frac{L^2}{2} \int_{-L/2}^{L/2} dz \phi_{fz}^* e^{-i\mu(z')} \phi_{zi}
\]

The integrals \( I_d \) and \( I \) can be evaluated analytically and the expressions are given in the appendix. Owing to the appropriate normalization of the wave functions, \( I_d, I_s \) and \( I \) are independent of \( L \) when \( L \to \infty \).

Note that the matrix element given in equation (31) is asymmetric in \( k_{xi} \). This can lead to an asymmetric photoemission where the number of electrons emitted with momentum \( k_x \) is different from electrons with number of electrons with \( x \) direction momentum \( -k_x \).

The matrix element for \( s \) polarized light can be given by

\[
M^2 = \frac{4K_1 |T_s|^2}{L^4} k_z^2 |i k_{yi}I|^2 h (k_{z i} - k_{xf}) h (k_{yi} - k_{yf})
\]

C. Calculation of the Matrix Elements

For \( p \) polarized light, using the Hamiltonian from equation (4) the matrix elements \( M = \langle \phi_f | H | \phi_i \rangle \) from equation (6) can be written as

\[
M = \langle \phi_{f1} | H | \phi_i \rangle = \frac{e \hbar A_0 T_p}{m_e c} \left\{ \sin \theta_t \frac{\partial}{\partial z} + \cos \theta_t \frac{\partial}{\partial x} + \sin \theta_t \delta (z') \phi_i \right\} \\
\]

where \( \phi_{f1} = \phi_f e^{-i\mu(z')} \)

FIG. 2. Example of the real component of the \( z \) dependent part of the initial bulk (a), surface (b) and final (c) wave functions. Here \( z_0 = 0.042 \) nm and \( s = 12.5 \).
D. Calculating the QE

The total QE can be written as sum of QE contribution from the bulk states (QE_{bulk}) and the surface state (QE_{ss})

$$QE = QE_{bulk} + QE_{ss}.$$ \hspace{1cm} (36)

QE_{bulk} can be given by

$$QE_{bulk} = \frac{R_{bulk}}{FL^2}$$ \hspace{1cm} (37)

where $R_{bulk}$ can be calculated from equation [3] with the integrations being carried over all possible initial bulk and final states. $F$ is the incident photon flux per unit area given by equation [3]

$$QE_{bulk} = \frac{K}{(2\pi)^2} \int d^3k_i \int d^3k_{z0} (|I_d + CI_s| \sin \theta_i + i k_{xi} I \cos \theta_i)^2 \times F(E_i)$$ \hspace{1cm} (38)

where $K = \frac{8(\hbar c)^3\alpha |T_{pi}|^2}{(2\pi)^2 (m_e c^2) \hbar \omega}$ and $\alpha$ is the fine structure constant. Note that we require $k_{xf} = k_x$ and $k_{yf} = k_y$ in order to match the transverse part of the final wave functions at the boundary.

In the limit as $L \to \infty$, $\hbar (\zeta) = 2\pi \delta (\zeta)$. Taking the limit as $L \to \infty$ and integrating over the final states we obtain

$$QE_{bulk} = \frac{K}{(2\pi)^2} \int d^3k_i \int d^3k_{z0} (|I_d + CI_s| \sin \theta_i + i k_{xi} I \cos \theta_i)^2 \times F(E_i)$$ \hspace{1cm} (39)

Note that $I$, $I_d$, $I_s$, $k_{z0}$ and $E_i$ are functions of $k_i$ and $k$. Integrating the $\delta$ functions in equation [40] we get $k_x = k_{xi}$, $k_y = k_{yi}$ and $k_z = k_{z0}$. These $\delta$ functions enforce the conservation of transverse momentum and energy during photoemission.

Similarly, QE_{ss} can be obtained using [38] as

$$QE_{ss} = \frac{2\pi K}{L} \times \int dk_{xi} \int dk_{yi} k_{z0} (|I_d + CI_s| \sin \theta_i + i k_{xi} I \cos \theta_i)^2 \times F(E_i)$$ \hspace{1cm} (41)

The normalization constant for the surface state ($N_{ss}$) is not dependent on $L$. Hence, for the surface state $I$, $I_d$ and $I_s$ are proportional to $\sqrt{L}$ even as $L \to \infty$. Thus, the surface state QE as given in equation [42] remains independent of $L$ as $L \to \infty$.

After writing $k_{xi}$ and $k_{yi}$ in cylindrical co-ordinates as $k_{xi} = k_r \cos \phi$ and $k_{xi} = k_r \sin \phi$; then integrating over $\phi$ the above expressions for QE_{bulk} and QE_{ss} can be written as

$$QE_{bulk} = \frac{2\pi K}{L} \int dk_r \int dk_{z} k_{z0} F(E_i) \times \left[ |(I_d + CI_s) \sin \theta_i|^2 + k_r^2 \frac{|I \cos \theta_i|^2}{2} \right]$$ \hspace{1cm} (43)

and

$$QE_{ss} = \frac{4\pi K}{L} \int dk_r k_{z0} F(E_i) \times \left[ |(I_d + CI_s) \sin \theta_i|^2 + k_r^2 \frac{|I \cos \theta_i|^2}{2} \right]$$ \hspace{1cm} (44)

respectively.

The QE for $s$ polarized light can be similarly calculated by using the appropriate matrix elements. The 3-D momentum distributions and the rms transverse momentum can also be calculated easily as shown in equation [10]

IV. RESULTS AND DISCUSSION

A. Spectral response

Figure 3 compares the spectral response measured from an Ag(111) surface to the result obtained from the photoemission model presented above, for $p$ polarized light at various angles of incidence.
In order to measure the QE, a commercially bought single crystal Ag(111) sample was prepared in an ultrahigh vacuum chamber with base pressure in the low $10^{-10}$ torr range. Several cycles of Ar ion bombardment and annealing to 500°C were performed until a sharp hexagonal LEED pattern was observed. The surface cleanliness was verified using Auger electron spectroscopy. The QE was obtained by measuring the photocurrent and the power of light incident on the sample surface. A laser based plasma lamp with a monochromator was used as a light source for the QE measurement. The spectral width of the light source was 2 nm FWHM.

All constants used for modeling the band structure to calculate the QE are given in table I. The optical constants ($n_i$ and $n_r$) for silver as a function of wavelength are well known. The surface constant $C$ and the electron-electron scattering length $d_{e-e}$ were obtained as a function of photon energy by extrapolating the values of $C$ and $d_{e-e}$ obtained from PES measurements. The scattering parameter $s$ is adjusted to match the QE experimental value. Figure 4 shows $\text{QE}_{\text{bulk}}$ and $\text{QE}_{\text{ss}}$ for $s = 1$ and $s = 12.5$. We can see that $\text{QE}_{\text{ss}}$ does not change significantly with $s$. The surface state is localized at the metal-vacuum interface. Hence the electrons excited from the surface state do not need to travel inside the metal to get emitted. This causes $\text{QE}_{\text{ss}}$ to be insensitive to $s$ or $k_d$.

In order to match the experimental data, $s$ needs to be set to a particularly large value of 12.5. This implies a much higher effective scattering rate than set by the electron-electron scattering lengths obtained from UV-PES data. The reason for this increased scattering is not clear.

1. Effect of Scattering

The decay constant of the final wave function $k_d$ takes into account the electrons that were excited by light but were unable to escape due to various scattering mechanisms while travelling towards the surface. The inelastic electron-electron scattering is the dominant scattering mechanism of excited electrons in metals. Hence we write $k_d = s/d_{e-e}$, where $d_{e-e}$ is the electron-electron scattering mean free path and $s$ is adjusted to match the calculated QE to the experimental value. Figure 4 shows $\text{QE}_{\text{bulk}}$ and $\text{QE}_{\text{ss}}$ for $s = 1$ and $s = 12.5$. We can see that $\text{QE}_{\text{ss}}$ does not change significantly with $s$. The surface state is localized at the metal-vacuum interface. Hence the electrons excited from the surface state do not need to travel inside the metal to get emitted. This causes $\text{QE}_{\text{ss}}$ to be insensitive to $s$ or $k_d$.

2. Vectorial Photoelectric Effect

Vectorial photoelectric effect is the variation of QE with the angle of incidence and polarization of incident light.

The QE for $p$ polarized light is given by equations and 14. In these equations, the term $|I_d + CI_s| \sin \theta_i$ corresponds to the QE contribution of the $z$ component of the polarization vector and the term $k_d^2 |I \cos \theta_i|^2$ corresponds to the QE contribution of the $x$ component of
the polarization vector. For the band structure and wave functions used here, $|\langle d_g + CL_d \rangle|^2 \gg k_r^2 \frac{|I|^2}{2}$. As a result, the photoemission from the Ag(111) surface is dominated by the $z$ component of the polarization vector (i.e., component perpendicular to the surface). Neglecting the contribution of the $x$ (parallel to surface) component, the QE can be written as

$$\text{QE} = K_p \left| \frac{T_p \sin \theta_t}{\cos \theta_i} \right|^2$$  (45)

where $K_p$ is a constant independent of the angle of incidence. Note that both $T_p$ and $\theta_t$ are dependent on the angle of incidence. Figure 5 shows that the experimentally measured angular dependence of QE for $p$ polarized light matches this calculation. This dependence is similar to the angular dependence of QE measured for several materials.\textsuperscript{11,12,31,32}

The spectral response calculated by the model at 0° angle of incidence is much smaller than the experimental value (see figure 3). At 0° angle of incidence only the $x$ and $y$ components of the polarization vector exist. This implies that the experimentally observed contribution of the $x$ and $y$ components of the polarization vector is larger than that calculated by the model. The assumption that the wave functions in the $x$ and $y$ directions are modeled by plane waves could be one possible culprit for this. Emission from parts of the band structure not modeled by the nearly free electron representation, many body photoemission effects like the hole state lifetime induces energy spread\textsuperscript{13} and the breakdown of the sudden approximation\textsuperscript{14} are other effects which may be responsible for this discrepancy. They may also be responsible for the large effective scattering parameter.

**B. Transverse Momentum Spread**

Figure 6 shows the rms transverse momentum expected from the Ag(111) surface. The rms transverse momentum has been calculated using equation 10 for angle of incidence equal to 60°. It can be seen that the rms transverse momentum initially decreases, reaches a minimum and then increases with increasing photon energy. At photon energies very close to threshold only electrons from the ring formed by the intersection of the surface state with the Fermi level are emitted. These electrons have a relatively high transverse momentum. At higher photon energies, electrons from the surface state with lower transverse momentum and lower energy can also be emitted along with the electrons from the surface state ring at the Fermi level. This causes the rms transverse momentum to initially reduce with increasing photon energy. This decline continues till the photon energy is sufficiently high to allow emission from the entire surface state. At this photon energy the rms momentum reaches a minimum. At higher photon energies, the electrons from bulk states which are located near the Fermi level and have a much higher transverse momentum are also emitted, causing the rms transverse momentum to increase again.

The smallest rms momentum measured from polycrystalline metal cathodes (which are typically used as electron sources) is limited by the room temperature to a value of 160 eV/c\textsuperscript{10} at the photoemission threshold. However, at the photoemission threshold the QE is also very low (in the $10^{-6}$-$10^{-7}$ range making polycrystalline cathodes unusable in this regime. At higher photon ener-
gies, the QE increases but so does the rms transverse momentum. In order to obtain a desirable QE greater than $10^{-5}$ the photon energy used has to be several 100 meV above threshold. This sets the rms transverse momentum practically obtained in electron guns to $\sim 350$ eV/$c$. According to our calculations, Ag(111) when operated at an angle of incidence of 60° in $p$ polarized light at 4.57 eV can act as a cathode with rms transverse momentum lower than 180 eV/$c$ and a QE as high as $5 \times 10^{-5}$. This shows that Ag(111) can act as a better photocathode the polycrystalline metals currently used as electron sources.

V. CONCLUSION

We have presented a 3-D one step model that allows us to calculate photoemission properties like QE and rms transverse momentum of emitted electrons from single crystal surfaces. Optimizing these photoemission properties can greatly improve the performance of electron source applications like FELs and UED.

Using the example of photoemission from Ag(111) we show that not only can this model calculate the spectral response from surface state without the use of any ad hoc parameters, but also explains the photoemission phenomena of the vectorial photoelectric effect accurately.

We also calculate the rms transverse momentum from an Ag(111) surface and show that in $p$ polarized light with a high angle of incidence, the Ag(111) surface can exhibit high QE along with a small rms transverse momentum, making it a much better cathode than the currently used polycrystalline metals. Upon integrating with other band structure and wave function calculation techniques like density functional theory, this methodology can be used to calculate the electron source relevant photoemission properties from any single crystal surface in order to identify ideal electron emitters from first principle calculations. Such a methodology is essential to screen for materials to identify good electron emitters.

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VII. APPENDIX

The analytic expressions to calculate several of the coefficients used in the wave function calculations are given below

$$\psi_{i,f} = \frac{(k^2 i (k_{zi}+p)z_0^2 - \frac{k^2}{2m_f} - E_{zi,zf} + V + E_0)}{V}$$

$$c_1 = \frac{[k_i + i (k_{zi} + p)] e^{-i(k_{zi}+p)z_0} + [k_i + i (k_{zi} - p)] e^{-i(k_{zi}-p)z_0}}{-k_i + i (k_{zi} + p)}$$

$$c_2 = \frac{[k_i + i (k_{zi} + p)] e^{-i(k_{zi}+p)z_0} + [-k_i - i (k_{zi} - p)] e^{-i(k_{zi}-p)z_0}}{-k_i + i (k_{zi} + p)}$$

$$t_{pk} = \frac{2i k_{zi}}{[i (k_{zf} + p + k_z) + k_d] e^{i(k_{zf}+p)z_0} + [i (k_{zf} - p + k_z) + k_d] e^{i(k_{zf}-p)z_0}}$$

$$1 + r_{pk} = \frac{2i k_{zi}}{[i (k_{zf} + p + k_z) + k_d] e^{i(k_{zf}+p)z_0} + [i (k_{zf} - p + k_z) + k_d] e^{i(k_{zf}-p)z_0}}$$

$$N = \frac{\sqrt{2}}{\sqrt{\left(\frac{k}{2}\right) (1 + \psi_i^2) + |c_1|^2}}$$ (assuming $L \rightarrow \infty$)

$$c_s = e^{i(k_{zi}+p)z_0} + \psi_i e^{i(k_{zi}-p)z_0}$$

$$N_s = \sqrt{2} \left[ \frac{e^{2(k_{zi}z_0)}}{2k_{zi}} \left( 1 + |\psi_i|^2 \right) + \frac{c_s e^{2(ip+k_{zi})}}{ip+k_{zi}} \right] + \left| \frac{c_s}{2k_{zi}} \right|^2$$

(46) (47) (48) (49) (50) (51) (52) (53) (54)
Note that the wave functions have been normalized to 2 in order to account for the electrons emitted from the equivalent $L$ point at $\left(-\frac{\pi}{a}, -\frac{\pi}{a}, -\frac{\pi}{a}\right)$. $z_0$ can be obtained by solving the following equation numerically

$$i \left( k_{2z} + p \right) e^{i(k_{2z} + p)z_0} + i\psi_s \left( k_{2z} - p \right) e^{i(k_{2z} - p)z_0} = -\kappa_s c_s$$

(55)

The analytic expressions for the integrals $I_d$ and $I$ used in the matrix element calculations are given below

$$I_d = \int dz \phi^*_{zf} \frac{\partial}{\partial z} \phi_{zi} = N\kappa c_2 \left( \frac{2ik_z}{k^2 + k_z^2} + \frac{1 + r^*_{pk}}{-\kappa_i + ik_z} \right)$$

(56)

$$+ N^*_{pk} \left[ i \left( k_{zf} + k_{zi} \right) e^{i(k_{zf} + k_{zi} + k_d)z_0} + \phi_i \left( k_{zf} + k_{zi} - 2p + k_d \right) e^{i(k_{zf} + k_{zi} + k_d)z_0} \right]$$

(57)

$$- c_1 \phi_i \left( -i \left( k_{zf} + k_{zi} + 2p + k_d \right) e^{i(k_{zf} + k_{zi} + k_d)z_0} + i \left( k_{zf} + k_{zi} \right) + k_d \right)$$

(58)

$$+ \phi_i \left( -i \left( k_{zf} + k_{zi} \right) + k_d \right)$$

(59)

$$I = \int dz \phi^*_{zf} \phi_{zi} = Nc_2 \left( \frac{2ik_z}{k^2 + k_z^2} + \frac{1 + r^*_{pk}}{-\kappa_i + ik_z} \right)$$

(60)

$$+ N^*_{pk} \left[ e^{i(k_{zf} + k_{zi} + k_d)z_0} + \phi_i \left( -i \left( k_{zf} + k_{zi} - 2p + k_d \right) e^{i(k_{zf} + k_{zi} + k_d)z_0} \right) \right]$$

(61)

$$- c_1 \phi_i \left( -i \left( k_{zf} + k_{zi} + 2p + k_d \right) e^{i(k_{zf} + k_{zi} + k_d)z_0} + i \left( k_{zf} + k_{zi} \right) + k_d \right)$$

(62)

$$+ \phi_i \left( -i \left( k_{zf} + k_{zi} \right) + k_d \right)$$

(63)

$$- c_1 \phi_i \left( -i \left( k_{zf} + k_{zi} \right) + k_d \right)$$

(64)

$$- c_1 \phi_i \left( -i \left( k_{zf} + k_{zi} \right) + k_d \right)$$

(65)

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