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Photoemission simulation for photocathode design: theory and application to copper and silver surfaces

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ABSTRACT

Obtaining a bright and low emittance electron beam directly from the photocathode is mandatory in order to design high performance free electron lasers (FELs). To achieve this goal a clear understanding of how the emission process is influenced by structure, morphology and composition of the photocathode surface is needed. This is difficult from an experimental point of view because often the atomic scale details of the surface whose emission has been measured are unknown. A predictive theoretical approach capable of determining the effects of surface structure on emission is therefore or great interest. A model to extend the well known three step model (as proposed by Berglund and Spicer) to surface calculations is discussed in this paper. It is based on a layer-by-layer decomposition of the surface electronic structure that can be calculated through reliable and efficient DFT calculations. The advantage of this approach with respect to other existing photoemission calculations is being able to correlate directly the photoemission to the electronic, atomic and chemical structure of the surface. The proposed approach retains, therefore, the simple chemical intuition in the study of surface modifications and their effect on the photoemission. The approach is validated in calculations of the emission from clean copper and silver surfaces. The ability of the model to simulate the change in photoemission in response to adsorbates is tested by simulating monolayers of oxygen, hydrogen and lithium on the copper (1 1 1) surface.

1. Introduction

Free electron lasers (FELs) are the state of the art in terms of light generation for time resolved spectroscopy [1,2]. In these devices, the lasing medium is the free electrons, which are emitted from a photocathode, accelerated by a linear accelerator and pass through an undulator to generate an intense photon beam. FELs give access to a broad wavelength range (THz to X-rays) and provide pulses of radiation of the order of the fs, in the time scale and six order of magnitude brighter than the previous sources [3–5]. Such short pulses of radiation allow the probing of the ultra-small (such as single molecule diffraction [5,6]) and of the ultra-fast (structural and electron dynamics [7]). The applications of the FELs radiation are many and varied covering different branches of the science such as biological structural studies (eliminating the need to crystallize the proteins/viruses [5,6]) and materials studies.

One of the main differences with respect to previous generation light sources is that FELs are single pass machines: electrons pass through the accelerator one time only introducing a dependance of the quality of the emitted radiation on the initial electron beam properties [8]. The quality of the emitted radiation (in terms of brightness and pulse length) depends on the quality of the electrons beam used to generate it. Therefore, photocathodes are a key component to modern accelerator systems and a broad international research programme [9] is now aimed at their improvement. An empirical approach has provided materials for the above mentioned applications; however, their efficiency is limited and a clear understanding of the emission mechanism and how it depends on material properties, would aid the rational design of new photocathodes.

Typically photoemission (PE) calculations are based either on just the bulk electronic structure or simplified models of the surface [10–14]. In order to achieve a rational design of new emitting materials it is necessary to understand how the surface structure influences the photoemission process. In this paper, a simple approach to compute photoemission from surfaces is presented. Firstly, density functional theory (DFT) calculations are performed on surface models. Modern DFT methods facilitates calculations on rather realistic models of surface environments that take into account their chemistry, morphology and structure. In order to

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connect the DFT surface electronic structure to the measured photoemission an extension of the well known three-step-model [15] to surface calculations is reported. A projection of the wave function onto pseudo atomic orbitals is used in order to calculate a layer-by-layer decomposition of the surface electronic structure. This approach is expected to reproduce satisfactorily the emission process while retaining the chemical intuition needed to understand the effect of morphology, composition and structure.

The above described method was tested on model systems, copper and silver clean surfaces as often used as emitting materials in photocathodes. Oxygen, hydrogen and lithium monolayers were simulated as additives on the copper (1 1 1) surface. These species were chosen in order to simulate the effect of atoms characterised by higher and lower electronegativity with respect to the copper substrate. Their effect on the band structure, work function (WF) and quantum efficiency (QE) spectrum is calculated and discussed.

In Section 2 details of the method are outlined. Photoemission simulations on copper and silver surfaces are reported in Section 3 as a test case.

2. Computational details

Electronic exchange and correlation were computed in the generalised gradient approximation (GGA) to density functional theory (DFT) using the PBE functional [16] and a plane wave (PW) basis set as implemented in CASTEP [17]. The variation in the total electronic energy per atom of the order of 10^{-5} eV was found for a plane wave energy cutoff of 500 eV and a Monkhorst–Pack [18] sampling of the Brillouin zone (BZ) of the bulk primitive cell of $14 \times 14 \times 14$. Tolerance on the geometry optimisation is set to be lower than 10^{-5} eV/atom and a Gaussian smearing of 300 K was used. Copper has an fcc structure (space group 225) whose optimised lattice parameter is 3.63 Å (experimental lattice parameter is 3.60 Å [19]). These parameters were used for all the calculations reported here. The accuracy of the copper bulk band structure was compared to GW calculations [20] and good agreement was found.

Surfaces are simulated using a thin slab model which has two-dimensional periodicity in the *xy* plane and is of finite thickness in the *z* direction. The slab is modelled in a 3D periodic cell with a vacuum space separating adjacent slabs. The surface formation energy was computed as a function of the vacuum gap spacing and the thickness of the slab. Variations of less than 10^{-3} J/m^2 from extrapolation to an infinite slab were achieved for a vacuum height of 15 Åand a thickness of 10 layers. For the 10 layer slab, the displacement of the central layer is found to be less than 0.1% of the bulk interlayer spacing. Furthermore, the electronic structure of the central layers of the slab, calculated using the projection of the density of states (PDOS) on the central atoms, reproduces that of the bulk crystal. This demonstrates that the mean field potential in the centre of the slab replicates that in a layer of the bulk crystal. Adsorption of oxygen, hydrogen or lithium to the surface of the 10 layer slab produces negligible changes in the displacement and electronic structure of the central layer. These tests suggest that the 10 layer slab model is adequate for the study of changes in the QE due to surface modifications.

Photoemission from the surface is sensitive to the formation of surface states. These states also play an important role in surface reactivity. The identification of surface states is facilitated by comparison of the band structure of a slab model with the surface projected band structure. A description of the technique used to obtain the projected band structure can be found in [21]. The bulk electronic states are defined within the first BZ of the bulk crystal as $\epsilon_i(\mathbf{k}) \equiv \epsilon_i(\mathbf{k}_{\|}, k_{\perp})$ where $\mathbf{k}_{\|} \equiv (k_x, k_y)$ and $\mathbf{k}_{\perp} \equiv (k_z)$. The electronic states of the 2D periodic slab are defined within the first BZ of the surface unit cell as $\epsilon_i(\mathbf{k}_{\|})$, where $\mathbf{k}_{\|} \equiv (k_x, k_y, 0)$. In the calculation of the surface projected band structure the same path chosen for the slab is used in the bulk calculation. This is achieved by creating a rotated bulk cell with two vectors in the surface plane in order to define suitable $\mathbf{k}_{\perp}$, which is sampled at different values and the different $\bar{\epsilon}_i(\mathbf{k}_{\|}, k_{\perp})$ are reported at $\mathbf{k}_{\|}$. An example of surface projected band structure of copper (1 1 1) and (1 0 0) surfaces in the region around Γ is reported in [22].

For a particular approximation of the surface electronic structure, the quantum efficiency is calculated here according to Eq. (1):

$$\mathrm{QE}(\omega, l) = \frac{\sum_{i=1}^{VBM}\sum_{f=WF}^{\infty}\int_{BZ}\left|\mathbf{M}_{i,f}^{\mathbf{k}}\right|^2 \delta\left(E(\omega) - \left(\epsilon_f^{\mathbf{k}} - \epsilon_i^{\mathbf{k}}\right)\right)\mathbf{W}_{i,l}^{\mathbf{k}}\mathbf{I}_l(\omega)\mathbf{esc}_{i,l}^{\mathbf{k}}\mathbf{H}(\mathbf{q}_{\perp} > 0)\frac{d\mathbf{k}}{(2\pi)^3}}{\sum_{i=1}^{VBM}\sum_{f=VBM+1}^{\infty}\int_{BZ}\left|\mathbf{M}_{i,f}^{\mathbf{k}}\right|^2 \delta\left(E(\omega) - \left(\epsilon_f^{\mathbf{k}} - \epsilon_i^{\mathbf{k}}\right)\right)\mathbf{W}_{i,l}^{\mathbf{k}}\mathbf{I}_l(\omega)\frac{d\mathbf{k}}{(2\pi)^3}} \tag{1}$$

This is an extension of Spicer's three step model [15] to surface simulations. The QE is defined through the energy of the incident photon ($\hbar\omega$) and the layer (l) from which the electron is emitted. The QE is measured in units of electrons/photon but, Eq. (1) gives a unitless result because it calculates the ratio between photons leading to emission with respect to the total number of photons reaching the surface. For the sake of simplicity, in the following, QE is reported as unitless. The integral is performed over the $\mathbf{k}$ points of the surface first BZ. In the denominator the summation involves all initial (i) and final states (f), whereas in the numerator only the final states leading to emission of the excited electron, *i.e.* the states above the vacuum level, are included. The model used in this work does not include any relaxation of the excited electronic state f. $\mathbf{M}_{i,f}^{\mathbf{k}}$ is an optical matrix element accounting for the coupling of the valence band i and the conduction band f at $\mathbf{k}$. Its square is the probability for the transition to occur between the two states:

$$\mathbf{M}_{i,f}^{\mathbf{k}} = \left\langle \psi_{\mathbf{k}}^{f} | \mathbf{u} \cdot \mathbf{r} | \psi_{\mathbf{k}}^{i} \right\rangle \tag{2}$$

In Eq. (2), $\mathbf{u}$ defines the polarization of the electric field of the incident light and $\mathbf{r}$ is the momentum operator. The delta function $\left[\delta\left(E(\omega) - \left(\epsilon_f^{\mathbf{k}} - \epsilon_i^{\mathbf{k}}\right)\right)\right]$ ensures the energy conservation in the process: only states whose energy difference matches the energy of the photon ($\hbar\omega$) are included in the summation. $\mathbf{W}_{i,l}^{\mathbf{k}}$ is the proportion (weight) of the density of states (DOS) attributed to layer l as estimated by projection of the DOS onto atomic orbitals (AO). The AO used here were those used in the construction of the pseudopotential (PP). The projection is used to measure the contribution of each layer to the initial state and is central to the layer-by-layer decomposition of the emission central to the application of Eq. (1). The efficacy of this approach for identifying the contribution of adsorbate induced surface states is demonstrated below. $\mathbf{I}_l(\omega)$ represent the intensity of light incident on the "lth" layer. The electron transport to the surface is taken into account by $\mathbf{esc}_{i,l}^{\mathbf{k}}$. This is the escape function for the electron excited from initial state i in $\mathbf{k}$ characterised by $\mathbf{W}_{i,l}^{\mathbf{k}}$. The escape function is estimated here using the universal mean free path, where the electron–electron scattering is the only phenomenon preventing electron emission [23]. This curve is determined by one parameter, the inelastic mean free path (IMFP) length which can be considered constant in the range of energy studied here. It was chosen to be 5.54 Å for copper and 6.13 Å for silver. These values are calculated as the average of those reported in the literature [24–28]. The heaviside step function $\mathbf{H}(\mathbf{q}_{\perp} > 0)$ ensures that only final state electrons characterised by a positive momentum along the direction perpendicular to the surface contribute to the QE. The $\mathbf{q}_{\perp}$ term defines the electron momentum in the vacuum. Since the momentum parallel to the surface ($\mathbf{k}_{\|}$) is conserved during the transition, $\mathbf{q}_{\perp}$ varies according to the energy of the final state f. $\mathbf{q}_{\perp}$ is determined by the conservation of energy such that: