Oxford Chemistry Primers: Foundations of Surface Science

Solutions for Chapter Three: Electronic Structure

3.1. Confirm that the integral in Eqn. 3.7 does indeed yield the expression in Eqn. 3.8, and demonstrate explicitly that the latter tends to the appropriate limiting value as $z \to 0$.

We are required to evaluate the integral from Eqn. 3.7 in Section 3.2

$$\rho(\mathbf{r}) = \frac{1}{2\pi^2}\int_0^{k_F}(k_F^2-\kappa^2)(1-\cos(2\kappa z))d\kappa$$

which we shall first simplify by multiplying out the brackets and introducing the substitution $u = 2\kappa z$, obtaining

$$\rho(\mathbf{r}) = \frac{1}{4z\pi^2}\left[k_F^2\left\{\int_0^{2k_F z}du - \int_0^{2k_F z}\cos u du\right\} - \frac{1}{4z^2}\left\{\int_0^{2k_F z}u^2 du - \int_0^{2k_F z}u^2\cos u du\right\}\right]$$

where we have made use of $du = 2zd\kappa$.

The first three integrals in this expression are straightforward to evaluate, and the fourth may be tackled via integration by parts. Eventually, we get

$$\begin{aligned}
\rho(\mathbf{r}) &= \frac{1}{4z\pi^2}\left[k_F^2\left\{[u]_0^{2k_F z} - [\sin u]_0^{2k_F z}\right\} - \frac{1}{4z^2}\left\{\left[\frac{u^3}{3}\right]_0^{2k_F z} - \left[2u\cos u + (u^2-2)\sin u\right]_0^{2k_F z}\right\}\right]\\
&= \frac{1}{4z\pi^2}\left[k_F^2\left\{2k_F z - \sin(2k_F z)\right\} - \frac{1}{4z^2}\left\{\frac{(2k_F z)^3}{3} - 4k_F z\cos(2k_F z) - ((2k_F z)^2-2)\sin(2k_F z)\right\}\right]\\
&= \frac{1}{4z\pi^2}\left[\frac{4k_F^3 z}{3} + \frac{k_F}{z}\cos(2k_F z) - \frac{1}{2z^2}\sin(2k_F z)\right]\\
&= \frac{k_F^3}{3\pi^2}\left[1 + \frac{3\cos(2k_F z)}{(2k_F z)^2} - \frac{3\sin(2k_F z)}{(2k_F z)^3}\right]\\
&= \rho_0 + 3\rho_0\left[\frac{\cos(2k_F z)}{(2k_F z)^2} - \frac{\sin(2k_F z)}{(2k_F z)^3}\right]
\end{aligned}$$

with $\rho_0 = k_F^3/3\pi^2$, matching Eqn. 3.8 (Section 3.2).

Evaluating this expression in the limit $z \to 0$ is a little tricky, as the denominators of both terms within the square brackets vanish, requiring us to find the difference between two infinities.

To make progress, let us expand both the sine and cosine functions as power series:

$$\begin{aligned}
\sin\theta &= \theta - \frac{\theta^3}{3!} + O[\theta^5]\\
\cos\theta &= 1 - \frac{\theta^2}{2!} + O[\theta^4]
\end{aligned}$$

We thus obtain

$$\begin{aligned}\rho(\mathbf{r}) &= \rho_0 + 3\rho_0\left[\left(\frac{1}{(2k_F z)^2} - \frac{1}{2!} + O[z^2]\right) - \left(\frac{1}{(2k_F z)^2} - \frac{1}{3!} + O[z^2]\right)\right] \\ &= O[z^2]\end{aligned}$$

which will plainly reduce to zero in the limit $z \to 0$ as required.

3.2. Nitrogen dioxide (NO_2) has a permanent dipole moment of 0.316 D per molecule in the gas phase. On a certain metal surface, molecules of NO_2 adsorb vertically, with their oxygen atoms toward the substrate, at a density of 10^{-9} mol.cm^{-2}. Assuming that the molecular dipole remains unaltered, and that no charge transfer occurs between the surface and the molecules, by how much (and in what direction) would the work function of the metal change?

Let us begin by calculating the dipole moment per unit area associated with the adsorbed NO_2 molecules. We do this by multiplying the molecular dipole moment by the given density and by Avogadro's number, yielding

$$p/A = -0.316 \times (10^{-9}) \times (6.022 \times 10^{23}) = -1.903 \times 10^{14}\ \mathrm{D.cm^{-2}}$$

where p and A represent, respectively, the dipole moment and the area across which it is distributed. We take the sign to be negative because the dipole moment of the molecule opposes that expected for a metal surface (i.e. the downward-pointing oxygen end of each molecule carries a partial negative charge and the upward-pointing nitrogen end a partial positive charge, as may be predicted from the relative electronegativities of the atoms).

Converting to SI base units, we obtain

$$p/A = -6.348 \times 10^{-12}\ \mathrm{C.m^{-1}}$$

where we have recognised that 1 D $= 3.33564 \times 10^{-30}$ C.m.

Using Eqn. 3.16 (Section 3.2) we find that the corresponding change in potential would be

$$\begin{aligned}\varDelta V &= \frac{e(p/A)}{\epsilon_0}\\ &= -\frac{(1.602 \times 10^{-19}) \times (6.348 \times 10^{-12})}{8.854 \times 10^{-12}}\\ &= -1.149 \times 10^{-19}\ \mathrm{J}\\ &= -0.72\ \mathrm{eV}\end{aligned}$$

which is to say that the work function of the surface would be reduced by just under three quarters of an electronvolt.

3.3. Scanning Tunnelling Microscopy of a Cu$\{111\}$ surface reveals decaying oscillations in the electron density in the vicinity of surface defects, with a characteristic spatial period of 15 Å. Ultraviolet Photoemission Spectroscopy on the same surface detects a feature lying within a gap in the projected bulk band structure, with a maximum binding energy relative to the Fermi level of 0.42 eV at the centre of the 1BZ. Assuming that both phenomena arise from one and the same Shockley surface state, estimate the effective mass of electrons occupying that state.

We start by recalling that a Shockley surface state will be associated with a parabolic band of the form described by Eqn. 3.18 (Section 3.3)

$$\epsilon = \epsilon_{min} + \frac{\hbar^2 k_{xy}^2}{2m^*}$$

and we shall choose, for convenience, to measure energies relative to the Fermi level. This means that states below the Fermi level will have negative values of ϵ, while those above the Fermi level will have positive values. The maximum binding energy (achieved at the centre of the 1BZ) will then simply be $-\epsilon_{min}$. Binding energies, it should be recalled, are conventionally regarded as positive for states lying below the Fermi level, and negative for those above, hence the need to invert the sign.

Based on the given photemission data, therefore, we may simply write $\epsilon_{min} = -0.42$ eV $= -6.729\times10^{-20}$ J.

Furthermore, scattering of Shockley surface states at defects is known to result in Friedel oscillations, visible in Scanning Tunnelling Microscopy images, with spatial periodicity given by π/k_F. In this expression, k_F represents the Fermi wavenumber of the surface state, not of the underlying bulk material. Inserting the given data, we find

$$k_F = \pi/15 = 0.21\ \text{Å}^{-1} = 2.1\ \mathrm{nm}^{-1}$$

for the wavenumber at which the parabolic band of the Shockley surface state crosses the Fermi level.

That is to say, when $k_{xy} = k_F$ we know that ϵ must be zero. Equivalently, we may write

$$0 = \epsilon_{min} + \frac{\hbar^2 k_F^2}{2m^*}$$

or

$$m^* = -\frac{\hbar^2 k_F^2}{2\epsilon_{min}}$$

into which we may substitute our known values of ϵ_{min} and k_F to obtain

$$m^* = -\frac{(1.055\times10^{-34})^2 \times (2.1\times10^9)^2}{2\times(6.729\times10^{-20})} = 3.647\times10^{-31}\ \mathrm{kg}$$

for the electronic effective mass. In terms of the mass of a free electron, $m_e = 9.109\times10^{-31}$ kg, this may conveniently be stated as $m^* = 0.40m_e$.

3.4. A schematic model for the ideal GaAs$\{111\}$ surface is shown below, but under mildly As-rich conditions it is thought that an ordered array of top-layer Ga vacancies would form, with one missing atom from each unit cell of the type shaded. Identify all dangling bonds within such a unit cell, and predict their occupancies, assuming that electrons are able to migrate between nearest neighbour atoms. Speculate on any likely consequences for relaxation of the remaining top-layer atoms.

Our first task is simply to count up the number of dangling bonds within the unit cell, which we shall do layer-by-layer and species-by-species. Before doing so for the defective surface, however, it will be sensible to start with the stoichiometric surface, as depicted in the schematic provided (and reproduced here as Fig. 1.a).

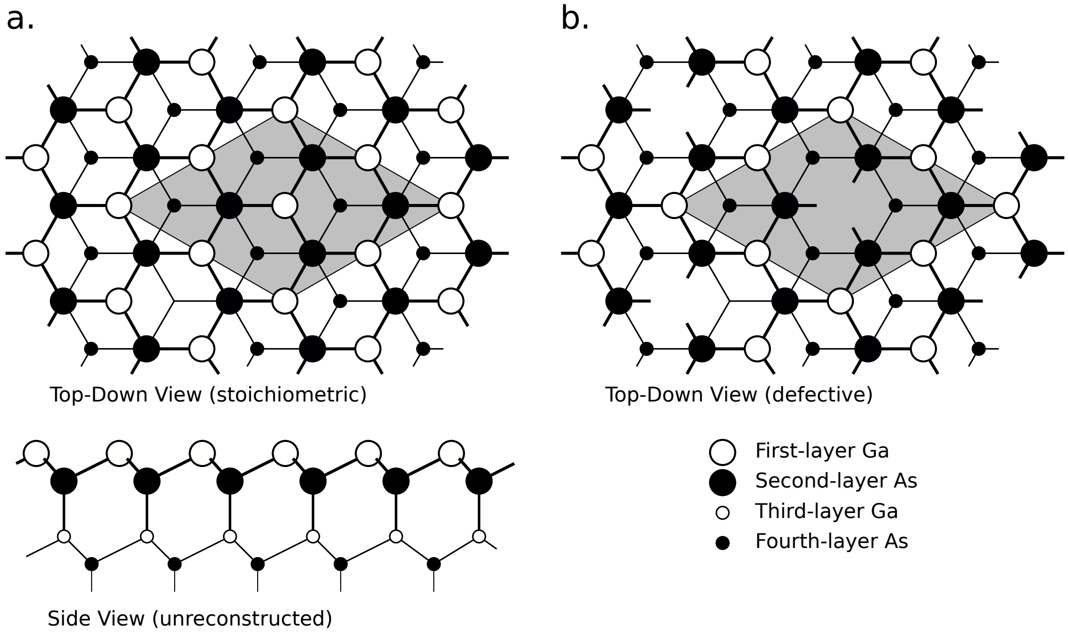

Figure 1: *Schematic views of stoichiometric and defective GaAs$\{111\}$ surfaces.*

In the first layer, then, we find that the unit cell contains four Ga atoms (one at the centre of the shaded cell in the image; four half-atoms on the edges of the shaded cell; and four quarter-atoms at the corners of the shaded cell). Each of these atoms makes three bonds that connect downward to As atoms in the second layer, implying that each also has one dangling bond pointing up out of the surface (assuming that four bonds would be the norm for a tetrahedrally coordinated compound). Thus there are four dangling bonds associated with first-layer atoms in the shaded unit cell.

Considering now the second layer, we find that the unit cell contains four As atoms (all lying wholly within the shaded cell in the image). Each of these makes three bonds that connect upwards to Ga atoms in the first layer, but also a fourth bond downwards to the third layer (although this latter is not visible in the image, because it is oriented vertically and thus hidden by a second-layer atom). There are, therefore, no dangling bonds associated with second-layer atoms, and indeed no further dangling bonds associated with deeper layers at all. For the stoichiometric surface, therefore, the total number of dangling bonds per shaded unit cell would be four, and all of these would relate to the first-layer Ga atoms.

Upon removal of one first-layer Ga atom from each shaded unit cell (Fig. 1.b) its dangling bond would no longer be counted, but three new dangling bonds would be formed – one associated with each of the three second-layer As atoms that previously bonded to the now-missing Ga atom. In total, the shaded unit cell would contain six dangling bonds, half located on the remaining first-layer Ga atoms, and half on these second-layer As atoms.

As for occupancies, it is usually helpful to start by counting electrons whilst applying the restriction that no redistribution between bonds is permitted at all. Since Ga and As have three and five valence electrons per atom respectively, it is expected that in bulk each bond receives 0.75 electrons from each Ga atom and 1.25 electrons from each As atom. The three dangling bonds associated with the first-layer Ga atoms would, therefore, contain 0.75 electrons each if no redistribution is allowed, while the three dangling bonds associated with the second-layer As atoms would contain 1.25 electrons each.

Relaxing our restriction on electron redistribution, on the other hand, we see that two possible scenarios could result in dangling bonds containing only zero or two electrons, which we have argued (see Section 3.3) should lower the surface energy. In one scenario, a charge amounting to 1.25e could be transferred from each second-layer As dangling bond to the dangling bond associated with one of its neighbouring first-layer Ga atoms – the first-layer Ga atoms would then each have a single completely filled dangling bond, while the three second-layer As atoms surrounding the vacancy would each have a single completely empty dangling bond. In the other scenario, a charge amounting to 0.75e could be transferred from each first-layer Ga dangling bond to the dangling bond associated with one of its neighbouring second-layer As atoms – the first-layer Ga atoms would then each have a single completely empty dangling bond, while the three second-layer As atoms surrounding the vacancy would each have a single completely filled dangling bond.

As to which of these two scenarios would be more likely, it should be noted that the second not only involves a smaller transfer of charge, but also involves transfer of electrons from the more electropositive species to the more electronegative. On both grounds, it is to be preferred over the first scenario.

Finally, we are asked to speculate upon any consequences for relaxation of the remaining top-layer atoms. Here, we might focus upon the fact that removal of electrons from a Ga dangling bond may favour a switch from an sp^3-like bonding arrangement to an sp^2-like alternative. That is, the remaining first-layer atoms may relax downwards (compared with their positions in the stoichiometric surface) to adopt a more nearly trigonal planar arrangement, in preference to a nominally tetrahedral one. Such a change may not necessarily be complete, as it will be limited by the build-up of strain in neighbouring bonds. In this connection, however, the presence of a first-layer vacancy might well also afford the second-layer atoms more leeway for lateral motion that may help to accommodate the tetrahedral-to-planar switch.

3.5. Ethylene epoxidation is a multi-billion dollar-per-annum industrial process, but the desired reaction

$$2C_2H_4 + O_2 \rightarrow 2C_2H_4O$$

is in competition with complete combustion

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

which is thermodynamically favoured. The consensus is that epoxidation is kinetically favoured in heterogeneous catalysis when adsorbed oxygen remains in molecular form, rather than dissociating on the surface, so the most effective catalysts are relatively inert coinage metals in preference to more reactive transition metals. Some dissociation of oxygen nevertheless occurs, however, even on the preferred silver catalyst. Adsorbed atomic chlorine is known to promote selectivity toward the desired reaction, although the overall activity of the catalyst is slightly reduced. Rationalise the role of the halogen promoter, with reference to the likely bonding modes of chlorine and oxygen with the metal surface.

In addressing the adsorption of molecular oxygen, a reasonable approach may be to consider its similarities to (and differences from) another diatomic species that we have examined in some detail, namely carbon monoxide. In Section 3.4, we focussed upon the HOMO and LUMO of CO, which were identified as the 5σ and $2\pi^*$ orbitals (the latter being doubly degenerate) and discussed four types of covalent interaction that these might have with orbitals from the surface. Two of these interaction types would lead to donation of electrons from the molecule to the surface, while two would lead to back donation from the surface to the molecule. The relative importance of each interaction may vary from surface to surface, and the net flow of electronic charge could, in principle, be in either direction.

Considering O_2 now, its molecular orbitals differ from those of CO because of the greater molecular symmetry, but nevertheless there will again be orbitals identifiable as being of σ and π type. Crucially, however, the O_2 molecule contains two more electrons than does the CO molecule, and these must be accommodated in its $2\pi^*$ orbitals. In the ground state, each of the $2\pi^*$ orbitals will accommodate one of these two electrons, and these unpaired spins will exist in a triplet configuration. From the perspective of frontier orbitals, therefore, the interaction of the molecule with a surface is most likely to involve these semi-occupied molecular orbitals rather than the fully occupied or wholly empty orbitals found at lower and higher energies respectively. We can reasonably imagine two scenarios, ionic or covalent, depending upon the position of these orbitals relative to the Fermi level of the surface and the degree to which they spatially overlap with substrate orbitals.

In the ionic scenario, an electron may be transferred wholly from the surface to a $2\pi^*$ orbital that remains otherwise unchanged from its gas-phase condition (electron transfer in the other direction is unlikely, given the electronegativity of oxygen). In the covalent scenario, one or both of the $2\pi^*$ orbitals may form bonding and antibonding linear combinations with substrate orbitals, with the net flow of electrons again probably dominated by back donation (on grounds of electronegativity). We do not have sufficient information from the question to really distinguish between these scenarios (nor even to predict whether the molecule will bind upright or horizontally on the surface) so describing the adsorption as being broadly polar-covalent in nature is probably the safest bet.[1] The only point we can be reasonably confident about is that the

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[1] For readers interested in going beyond what may be inferred from the question, a sensible starting point for further study might be the recent review article by Montemore *et al* [Chem. Rev. 118, 2816 (2018)]. Spoiler Alert: the molecule is thought

molecule will probably develop a net negative charge, associated with increased occupancy of one or both of its $2\pi^*$ orbitals. This, in turn, will weaken the O–O bond to some degree (because these orbitals are of antibonding character) tending to lower the barrier toward dissociation.

The adsorption of chlorine is comparatively much simpler, not least because we are told that it exists at the surface in adatomic form. In this case, we can count upon it being very electronegative, and possessing a semi-occupied orbital that falls clearly below the surface Fermi level. Transfer of an electron from substrate to adsorbate can then be predicted with some confidence. Accordingly, we see that molecular oxygen and atomic chlorine are, to some degree, in competition for whatever electrons the surface can supply.

One common way of expressing this competition for electrons is first to view the adsorption of chlorine as increasing the surface dipole, and hence increasing the work function, in a manner essentially opposite to the example of alkali metal adsorption described in Section 3.4. Electron transfer from the surface to oxygen molecules is then understood to take place in the context of this increased work function. Granted, the electrons involved do not have to surmount the entire work function, since they are not being emitted all the way to the vacuum level, but clearly an increase in work function will serve to reduce the eventual occupancy of the $2\pi^*$ orbitals. This will have the effect of reducing the heat of adsorption for O_2, since the bonding interaction with the surface is thus reduced, but should also suppress dissociation, since the same interaction is responsible for weakening the intramolecular bond. We may therefore anticipate that the total surface coverage of oxygen will be reduced (and simple blocking of possible adsorption sites by atomic chlorine may also play a role in this) leading to a reduction in overall activity. On the other hand, however, the selectivity should increase, as a greater proportion of adsorbed oxygen remains in molecular, rather than adatomic, form.

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typically to bind more-or-less horizontally, while the exact degree of its negative charge remains somewhat contentious and probably depends upon which particular silver surface is involved.