5 Studying the Details of the Electron–Electron Interaction in Solids and Surfaces

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5.1 Introduction

Recently substantial experimental advances have been achieved in the energy-, spin- and angular-resolved detection of electron pairs that are simultaneously excited from solid surfaces by laser excitation by electrons or photons beams [1-14]. This process, which is for electron impact also called (e,e2) (one electron in, two electrons out) is visualized schematically in Figure 5.1. The (e,e2) studies from surfaces can be categorized in two broad classes: (1) the transmission and (2) the reflection mode experiments [1, 2]. The transmission mode experiments are reviewed in Chapter 7. In this kind of experimental arrangement the incoming energetic electron transmits a free-standing thin film. The two ejected electrons are detected on the side of the films that does not contain the incident beam, i.e. both first-order electrons propagate in the forward direction with respect to the incoming beam. A typical reflection mode setup is shown schematically in Figure 5.1. All incoming and outgoing vacuum electrons are detected in the same half plane. The information obtainable from the (e,e2) measurements is quite different depending on the experimental arrangement and on the energies and momenta of the vacuum electrons, as discussed below.

5.2 General Considerations

To appreciate the significance of the (e,e2) process it is instructive to inspect the structure of the (e,e2) transition probability $W(k_{o}, k_{1}, k_{2})$:

$$W(k_{o}, k_{1}, k_{2}) = \sum_{k_{i}} \langle k_{o} k_{1} k_{2} | T_{e-e}(\omega_{e}) | k_{o} k_{1} k_{2} \rangle^{2} \delta(E_{i} + E_{f} - E_{0} - \epsilon_{i}). \tag{5.1}$$

Here $E_{i}, E_{f}$ are the energies of the emitted electrons that are described by the final-state wavefunctions $\psi_{k_{o}}, \psi_{k_{1}}$ (or the electron's wave vectors). The initial electronic states of the target are characterized by the single-particle orbitals $\psi_{k_{2}}$, where it is the Bloch wave vector and the index $i_{f}$ characterizes all other quantum numbers needed to specify the state of the surface. The incoming electron beam is described by the wavefunction $\psi_{k_{o}}$. The operator $T_{e-e}(\omega_{e})$ induces the transition from the initial state $|k_{o} k_{1} k_{2}\rangle$ into the final state $|k_{o} k_{1} k_{2}\rangle$, while conserving the total energy.

5.3 Results and Interpretations

Equation (5.1) can be re-written (exactly) as the expectation value of an effective operator $M$, where

$$W = \langle \langle k_{o} k_{1} k_{2} | M | k_{o} k_{1} k_{2} \rangle \delta(E_{i} + E_{f} - E_{0} - \epsilon_{i}) \rangle \tag{5.2}$$

$$M = \sum_{k_{i}} \langle k_{o} k_{1} k_{2} | T_{e-e}(\omega_{e}) \rangle \langle k_{o} k_{1} k_{2} \rangle \delta(E_{i} + E_{f} - E_{0} - \epsilon_{i}) \tag{5.3}$$

To illustrate the kind of information that can be gained from an (e,e2) experiment we proceed as follows: If in Eq. (5.3) the transition operator $T_{e-e}$ does not depend on the properties of the occupied states, we operate within the Born-Oppenheimer approximation (i.e. we start from an asymptotic uncorrelated state $|k_{o} k_{1} k_{2}\rangle = |k_{o}\rangle \otimes |k_{1}\rangle \otimes |k_{2}\rangle$ and then write $M$ as

$$M = T_{e-e}(\omega_{e}) \langle k_{o} k_{1} k_{2} | \langle k_{o} k_{1} k_{2} | T_{e-e}(\omega_{e}) \langle k_{o} k_{1} k_{2} \rangle \delta(E_{i} + E_{f} - E_{0} - \epsilon_{i}) \rangle \tag{5.4}$$

$$= \int \frac{dp_{o} dp_{1} dp_{2}}{(2\pi)^{3}} \langle k_{o} k_{1} k_{2} | T_{e-e}(\omega_{e}) \langle k_{o} k_{1} k_{2} \rangle \delta(E_{i} + E_{f} - E_{0} - \epsilon_{i}) \rangle \tag{5.5}$$

In the second line of this equation we inserted a complete set of plane waves $\langle p_{o} | \psi_{p_{o}} \rangle$. The expression in the wave bracket is the non-local spectral density which is expressible in terms of the imaginary part of the retarded Green's function of the surface $G_{R}(q, q')$. The latter is evaluated at the energy $E = (E_{i} + E_{f}) - E_{0}$ that is determined experimentally (all energies are measured with respect to the vacuum level). Inserting Eq. (5.4) into Eq. (5.5) one deduces that

$$W = \int \frac{dp_{o} dp_{1} dp_{2}}{(2\pi)^{3}} \langle k_{o} k_{1} k_{2} | T_{e-e}(\omega_{e}) \langle k_{o} k_{1} k_{2} \rangle \delta(E_{i} + E_{f} - E_{0} - \epsilon_{i}) \rangle \tag{5.6}$$

$$= \langle T_{e-e}(\omega_{e}) \rangle \langle k_{o} | \psi_{k_{o}} \rangle \langle \psi_{k_{o}} | T_{e-e}(\omega_{e}) | k_{o} \rangle \langle k_{1} | \psi_{k_{1}} \rangle \langle \psi_{k_{1}} | T_{e-e}(\omega_{e}) | k_{1} \rangle \langle k_{2} | \psi_{k_{2}} \rangle \langle \psi_{k_{2}} | T_{e-e}(\omega_{e}) | k_{2} \rangle \tag{5.7}$$

5.3 Results and Interpretations

The usefulness of the exact mathematical exercise presented above becomes now apparent: Equation (5.7) contains three important physical quantities: 1. The hole non-local spectral density $\langle \psi_{k_{o}} | T_{e-e}(\omega_{e}) | \psi_{k_{o}} \rangle$. 2. The electron-electron interaction $T_{e-e}$ and 3. The correlated electron-electron wavefunction $\psi_{k_{o}}$. Choosing the appropriate experimental set-up one can focus on each of these quantities separately. E.g., if we assume that $T_{e-e}$ depend only on

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1 This is not always the case, e.g. for certain elements $T_{e-e}$ is spin dependent (for example due to spin-orbit coupling) and hence it depends on the spin quantum numbers of the electrons' states of the surface.
Figure 5.2: The energy of an alpha-particle after passing through a solid angle of \(\theta_{\alpha,\alpha} = 30^\circ\) for various values of \(E_{\text{lab}}\) and \(E_{\text{out}}\). The incident energy is fixed at 200 eV, and the secondary electron energy is varied between 0 and 200 eV. The angular distribution shows a peak at \(\theta_{\alpha,\alpha} = 30^\circ\), indicating strong secondary emission at this angle. The data are for a specific substrate material.

Figure 5.3: Example data for the electron-electron interaction in a solid: (a) shows the energy distribution of electrons emitted from a surface as a function of primary electron energy. The data are for a specific substrate material.

The angular distribution of secondary electrons is given by:

\[
\frac{d^2\sigma}{d\Omega} = \frac{1}{2}\pi E_{\text{lab}}^2 \frac{dE_{\text{out}}}{d\omega} \sin^2 \theta_{\alpha,\alpha}
\]

where \(d^2\sigma/d\Omega\) is the differential cross-section, \(E_{\text{lab}}\) is the incident energy, \(E_{\text{out}}\) is the secondary electron energy, and \(\theta_{\alpha,\alpha}\) is the angle between the incident and secondary electron vectors.

The secondary electron intensity is given by:

\[
I_{\text{out}} = \frac{1}{2}\pi E_{\text{lab}}^2 \frac{dE_{\text{out}}}{d\omega} \sin^2 \theta_{\alpha,\alpha}
\]

where \(I_{\text{out}}\) is the intensity of secondary electrons, \(dE_{\text{out}}/d\omega\) is the secondary electron energy distribution, and \(\theta_{\alpha,\alpha}\) is the angle between the incident and secondary electron vectors.

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### Results and Interpretations

#### Solute Distribution in Ionic Liquid Solutions

- **Figure 5.2:** The solute distribution in ionic liquid solutions can be explored through the study of the effective distribution coefficients, as noted in Table 5.2, which highlight the solute-ionic liquid interactions. These interactions are crucial for understanding the thermodynamic properties of the solutions.

- **Table 5.2:**
<table>
<thead>
<tr>
<th>Solvent Type</th>
<th>Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous</td>
<td>0.85</td>
</tr>
<tr>
<td>Ionic Liquid</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The high distribution coefficient values for the ionic liquid suggest a strong interaction between the solute and the solvent, leading to increased solute solubility in the ionic liquid compared to the aqueous solution. This is in line with the theoretical predictions of the model used in the calculations.

#### Electrochemical Reaction Kinetics

- **Figure 6.4:** The electrochemical reaction kinetics are depicted in Figure 6.4, showing the relationship between the reaction rate and the applied voltage. The results indicate a linear increase in reaction rate with increasing voltage, as expected for a first-order reaction process.

- **Equation 6.1:**
  
  \[ r = k \times \text{voltage} \]

- **Discussion:** The linear relationship is consistent with the theoretical predictions of the model, validating the assumptions made in the reaction mechanism development.

#### Conclusion

The study provides a comprehensive understanding of the solute distribution and electrochemical reaction kinetics in ionic liquid solutions. These findings are crucial for the development of new ionic liquid-based technologies, such as electrochemical capacitors and ion-selective membranes.
Figure 5.4: The same as in Figure 5.2a, however the emission angles of the two electrons are varied as shown on the light-reversed panels. The target is a Cu(001) single crystal.

Figure 5.3 cannot occur in an atomic or a molecular target (for an atomic or a molecular system usually one single discrete bound state is involved in the process and the wave vector is not a good quantum number). In addition, from phase-space consideration one can show [11] that the electron-pair emission probability scales as $k_1 k_2$. Therefore, all the spectra shown above vanish when $E_1 = 0$ or $E_2 = 0$. This is not the case for an atomic or a molecular target. The reason for this is that, in contrast to metal surfaces, the single electron density of states in an atomic target diverges at threshold as $1/E$. Therefore this divergence is canceled out by the phase-space factor $k_1 k_2$ and the $(2e)$ energy-sharing spectra for atomic or molecular targets are finite when $E_1, E_2 \neq 0$.

The ordering of the crystal potential also has a profound influence on the electron-pair energy spectra. A spectrum of a single electron scattered from an ordered multi-center potential shows well-known diffraction patterns [16, 17]. In monog, two electrons can also be diffracted from the crystal potential, resulting in electron-pair diffraction [3]. As observed in Figure 5.3, when the initial total wave vector of the electron pair $\mathbf{k}_1 + \mathbf{k}_2$ is changed by a multiple of a reciprocal lattice vector, diffraction peaks appear. In the experiment these peaks are less pronounced than the finite experimental resolution [16]. Examples of the pair-diffractions are found in Refs. [3, 18]. In this context it should be remarked that the interaction of the electrons with the crystal potential is usually assumed to be of a single-particle nature that the potential has a multi-center character. Thus, in single-particle terms one can say that one of the electrons is diffracted from the crystal potential and subsequently collides with the other electron. Since the two electrons can exchange momenta, the single particle diffraction peaks are then diffused. On the other hand, other peaks appear due to the common..
vation of the electron pair (parallel wave vector model) of a reciprocal lattice vector, as expressed by Eq. (5.7). This argument does not rely on which scattering process occurs first. The key point here is that the electron-pair diffraction depends crucially on the momentum transfer within the electron pair and hence it is a direct manifestation of the interaction between the two electrons. This is quite the opposite situation to the diffraction process of a single particle from a crystal potential which is hardly dependent on the electronic correlation.

5.4 Conclusions

The aim of this chapter is to present a small fraction of the rich phenomena that occur when an electron pair is excited from a surface. Here we have chosen to focus on the interpretation of the spin-averaged scattering from clean surfaces. The (e,2e) experiments and theories have evolved historically to include the study of ferromagnets, semiconductor, wide-band gap insulators, alloys, clusters and adsorbates. The results of some of these studies are reviewed in Ref. [19] where further references can be found.

References