Sensing the electron–electron correlation in solids via double photoemission

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We discuss the electron pair emission from surfaces upon the absorption of a single photon, also called double photoemission (DPE). This experiment is particular sensitive to the electron–electron interaction, because for independent electrons the DPE intensity is zero. We outline the experimental development of this technique over the past decade. Going beyond the mere detection of pairs we advanced the instrumentation. Now we are able to measure the kinetic energies and emission angles of a wide angular acceptance. We will show how the available energy is distributed among the electrons and how the angular distributions look like. The latter enabled us to make contact to an important concept of modern solid state theory, namely the exchange–correlation hole. We demonstrate that the exchange–correlation hole manifests itself in a depletion zone of the coincidence intensity around the fixed emission direction of one electron. The experiments were performed at the synchrotron facilities BESSY I and BESSY II.

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1 Introduction In electronic systems which contain more than one electron the interaction between electrons plays an important role. The origin of the mutual influence is due to the Pauli principle and the Coulomb interaction. The additional term in the Schrödinger equation describing the electron-electron interaction makes an analytical solution impossible. Therefore one has to resort to approximations and appealing ones are those, which employ an effective single particle picture. As an example one may consider the He-atom, the simplest two-electron system besides the H₂ molecule. If one completely neglects the electron-electron interaction in the description one obtains for the energy required to double ionize a He-atom a value of 108.8 eV. For this determination we make use of the known exact solution of the H-atom. This value is different by a large margin from the experimental observation. Using photons for excitation to ionize the He-atom and to liberate the two electrons an energy in excess of 79 eV is required. An improved description can be formulated if one makes use of the intuitively clear assumption that each electron is located near the nucleus. This in turn means that each electron does not experience the full Coulomb poten-

tial of the nucleus. We expect that effectively each electron will screen to some extent this bare Coulomb potential. Consequently one replaces the nuclear charge Z = 2 by Z = 2 - S, where the parameter S describes the amount of screening. By doing so we have included the electron– electron interaction in an approximation, while maintaining in a formal sense an independent electron picture. For this model an analytic solution is possible, again we make essentially use of the known result for the H-atom. Adopting a value of S = 0.656 one obtains good agreement with experiment as far as the energy required to ionize and double ionize the He-atom is concerned.

The treatment of an electronic system with a large number of electrons becomes rapidly more complex than the atomic case. There exist a variety of so-called many body effects, which are the manifestation of the electron– electron interaction. Ferromagnetism and superconductivity may suffice as examples. In a ferromagnet the spins at different lattice sites align parallel to each other, which is due to the exchange interaction between the electrons, which is essentially the Coulomb interaction modified by the Pauli principle. Likewise electrons forming a Cooper



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pair interact (within the BCS theory) via electron-phonon coupling.

Nevertheless, we start to discuss the simplest model for describing a metallic solid, namely the free electron gas. There one neglects the Coulomb interaction and hence the electrons move independently from each other. Despite the fact that this picture has to be a crude approximation, it contains very important features. For the development of the solid state theory it was a great success of this model that it was able to predict the temperature dependence of the electronic specific heat correctly. In context of our work another feature of the free electron model is of relevance. Although the global charge distribution is uniform within this model it turns out that the charge distribution around each electron is not uniform. In order to elaborate on this it is now instructive to pose the question what is the probability to find one electron at location r_1 , while the other is at r_2 and how does it vary with the difference vector $r_1 - r_2$ between them. The free electron gas is isotropic, hence only the length of the distance vector $r = |\mathbf{r}_1 - \mathbf{r}_2|$ is of relevance. We have to distinguish parallel $(\uparrow\uparrow)$ and antiparallel $(\uparrow\downarrow)$ alignment of spins. The entity we are looking for is the so-called pair correlation function $g_{\uparrow\uparrow}(r)$ and $g_{\uparrow\downarrow}(r)$, respectively. For parallel spins we know immediately from the Pauli principle that the two electrons with the same spin cannot be at the same location. For very large distances we expect to find with certainty another electron, after all there are electrons in this model, which are described by plane waves. Consequently what is left to do is to determine the length scale over which the probability rises from 0 to 1. The calculation of $g_{\uparrow\uparrow}(r)$ is straightforward and was first reported by Wigner and Seitz [1], it can be found in solid state physics textbooks, e.g. [2]. It turns out that the natural variable is the term $k_{\rm F}r$ in which $k_{\rm F}$ is the Fermi momentum, the result for $g_{\uparrow\uparrow}$ is:

$$g_{\uparrow\uparrow}(x) = 1 - 9 \frac{(\sin(x) - x\cos(x))^2}{x^6}$$
(1)

with $x = k_{\rm F}r$. We have plotted this result in Fig. 1 as the solid line. We notice that $g_{\uparrow\uparrow}$ rapidly increases and at about x = 4 has essentially approached one. We recall that for metals typical values for $k_{\rm F}$ are of the order 1–2 Å⁻¹. This means that over a length scale of a few nearest neighbors $g_{\uparrow\uparrow}(r)$ has the value 1. For antiparallel spins the result for $g_{\uparrow\downarrow}(r)$ is particularly simple since it has a constant value of 1, which is drawn as dashed line in Fig. 1. The Pauli principle does not prohibit two electrons to be at the same location if the spins of the electrons are different. From this evaluation of the pair correlation function it becomes apparent that each electron is surrounded by a reduced electron density compared to the global average of the free electron gas. The area of the shaded region of Fig. 1 is a measure of this and it turns out that exactly one electron charge is missing, which is also known as the exchange hole. From this we learn an important fact, namely that each electron is effectively screened for distances

more than a few lattice constants away. If we consider an electronic system including the Coulomb interaction we expect that also electrons with antiparallel spins to avoid each other. The schematic behavior of the pair correlation as a function of the distance between the electrons is depicted in Fig. 2, where we made use of the ideas suggested by Slater [3]. As for the case of non-interacting electrons $g_{\uparrow\uparrow}(r)$ vanishes if r = 0, while $g_{\uparrow\downarrow}(r)$ is strongly reduced from the value 1. It is intuitively clear that it is energetically not favorable for electrons to be close to each other, although it is not forbidden as for the case of electrons with parallel spins. The average of the $g_{\uparrow\uparrow}(r)$ and $g_{\uparrow\downarrow}(r)$ distributions is shown in panel b) of Fig. 2. This curve describes the probability to find an electron of any spin around a fixed electron and the net result is that each electron is surrounded by a reduced electronic charge. The shaded area is a measure of the missing charge and one finds that exactly one electronic charge is missing. In this context we talk about the exchange-correlation (xc) hole. From this discussion we learn that a more appropriate description of the electron-electron interaction is to use a screened Coulomb potential of the form $V \sim (1/r) e^{r/\lambda}$ rather than the bare Coulomb interaction. In this context the screening length λ is a measure of the lateral dimension of the xc-hole. This concept of the exchange-correlation hole was introduced in seminal papers by Wigner & Seitz and Slater more than 70 years ago [1, 3, 4]. It is important to point out that this concept is an integral part of modern solid state theory. Within the framework of the density functional theory one employs often the so-called local density approximation (LDA). Essentially all many-body effects of the interacting electron system are cast into the so-called exchangecorrelation energy functional. For this one usually uses the expression for an interacting electron gas, which incorpo-



Figure 1 Pair correlation function g(x) for the free (noninteracting) electron gas, where *x* equals $k_F r$. The solid line shows the dependence for parallel spins, while the dashed line is for antiparallel aligned spins. The shaded area is a measure of the charge missing around the vicinity of an electron. This amount equals exactly one elementary charge and is called the exchangehole.



Figure 2 Schematic behavior of the pair correlation function g(r) for an interacting electronic system following the idea of Slater [3]. In panel a) we plot g(r) for parallel (solid curve) and antiparallel (dashed curve) spin alignment. In panel b) we show the average of the two functions. The shaded area is a measure of the charge missing around the vicinity of an electron. This amount equals exactly one elementary charge and is called the exchange– correlation hole.

rates the exchange–correlation hole. There are strong theoretical efforts underway, which aim to derive a more accurate description beyond the LDA. Central to these activities is the pair correlation function [5-7].

The properties of matter are ultimately determined by the electronic properties. A spectroscopic means to study the electronic properties is photoemission. In particular, angle-resolved energy distributions allow comparison with band structure calculations. Usually, one discusses peaks in the intensity distributions within an effective singleelectron picture. Recent advances in the angle and energy resolution have made it possible that photoemission allows to observe effects due to many-body interactions. These so-called kinks in the E(k) curve or dispersion are the result of the electron-electron interaction or the coupling to other degrees of freedom [8]. Electrons will not move independently through a solid, but will experience a mutual influence in their motion. Clearly the route, which goes beyond single electron spectroscopy will reveal aspects of the electron-electron correlation not accessible by photoemission. An experimental access to study the electronelectron interaction is to use the technique of double photoemission (DPE), which is absorption of a single photon and the simultaneous emission of an electron pair. The

basic facts. In the absence of an electron-electron interaction the electronic system consists of independent electrons, consequently the description with single electron wave functions is allowed, for example via a Slater determinant. If an electron of such a system absorbs a photon and is ejected other electrons will not "feel" this and the emission of a second electron (or more electrons) will not occur, although it is energetically possible if the photon energy is higher than twice the work function. This intuitive picture can be cast into a theoretical framework, which shows that within the dipole approximation a finite electron-electron interaction leads to a finite DPE intensity [9]. With this in mind it becomes clear that DPE is particular sensitive to the electron-electron interaction. Moreover, a theoretical study on the DPE emission from a Cu(100) surface clearly showed that the exchange-correlation hole manifests itself in the angular distribution of the coincidence intensity [10-12]. The power of DPE has also been recognized in studies of atomic or molecular targets [13-15]. As it turns out the first DPE experiment on solids was performed on alkali samples in the year 1970 by Gazier and Prescott [16]. The next experimental result, obtained from noble gas films, appeared in 1987 [17, 18]. In both of these early experiments it was demonstrated that the process of electron pair emission upon photon absorption does exist, though no discrimination with respect to energy was performed at the time. In order to make DPE from surfaces a viable tool major developments are necessary to obtain energy and angular distributions. Our recent achievements are the subject of this review. In particular, we will show that we are able to observe the manifestation of the exchangecorrelation hole.

power of the tool can be understood by considering some

2 General aspects of the experiment The recent success has been only possible because of significant technical improvements of the instrumentation. The results we are going to present in this review have been obtained with different generations of machines. In common to all is the use of the time-of-flight (TOF) technique together with a fast coincidence circuit, which ensures the detection of electron pairs only. A TOF set-up needs a pulsed excitation source for which we employed the single-bunch mode of the BESSY I and BESSY II storage rings at the beamlines TGM 4 and CP-NIM. The storage ring bunch marker was used as a time reference in order to determine the kinetic energy of the electrons from the TOF spectra. We quote the kinetic energy with respect to the vacuum level. As we go along, we will briefly describe the set-up used, a more detailed account can be found in the original publications. A few general remarks of electron pair detection are in order. The process we are interested in is the emission of a pair upon absorption of a single photon. It is important to realize that it is not possible that each light pulse hitting the sample contains exactly one photon. The distribution of the number of photons in a light pulse is of statistical nature and is described by the Poisson statistics. The only adjustSolidi Solidi

ment possible is to fix the average number of photons in the light pulses. Suppose that we adjusted the primary intensity such that the average number of photons per light pulse is 1. For this example we find for the percentage of pulses containing 0,1 or 2 photons the values 36%, 37% and 19%, respectively. Of course the light pulse can contain also more than 2 photons, but we can ignore these in the following. The important fact is that besides the genuine pair emission (absorption of a single photon), which we term "true" coincidences, also two independent single photoemission processes are possible, whereby the uncorrelated electron pair also will trigger the coincidence circuit. In this context we talk about "random" coincidences. We know that the single photoemission process is much more likely to occur in contrast to the DPE process. An usual experimental observation is that the single photoemission count rate is about a factor of 1000 higher than the coincidence rate as observed in the pioneering experiment by Gazier and Prescott [16]. Therefore one has to pay attention to reduce the number of "random" coincidences. The obvious way is to reduce the primary intensity. As an example, we assume now that on average each light pulse contains 0.01 photons. Via Poisson-statistics we have for the percentage of pulses contain 0,1 and 2 photons values of 99%, 0.99% and 0.0049%. We immediately notice that the number of pulses containing a single photon is by a factor of 200 higher than the number of pulses containing 2 photons. The drawback is that 99% of the pulses are empty hence one has to operate at a low primary flux, which in turn means that the "true" coincidence rate is low, too. We achieve with an apparatus with large angular acceptance values up to 50 coincidence counts per sec. We point out that the low count rates are not due to a deficiency of the experimental set-up, but due to the fact that the xc-hole effectively screens the electrons. This is the reason why our coincidence experiments require data accumulation times of the order of weeks to obtain sufficient statistics.

3 Results

3.1 Energy distributions of electron pairs If electron pairs are emitted it is of great interest to know how the available energy is shared among the electrons. For example, is there a tendency for both electrons to have similar energies or are they rather different? The first experimental account on solids was given by Hermann et al. [19], who investigated Cu(100) and Ni(100) surfaces, respectively. A sketch of the apparatus used is depicted in Fig. 3. In brief, linearly polarized light hits the sample along the surface normal. The light polarization is in the drawing plane as indicated by the arrow. Emitted electrons are registered via a pair of detectors arranged symmetrically with respect to the surface normal, such that electrons with an emission angle of 40° can be detected. In Fig. 4 we display the 2D-Energy distribution from a Cu(100) surface, where the photon energy was fixed to 45 eV. For the process of DPE energy conservation has to hold. We write for the sum en-



Figure 3 Sketch of the experimental apparatus used by Herrmann et al. [19]. Linear polarized light impinges normal to the surface. The polarization direction is in the drawing plane.

ergy of a pair $E_{sum} = E_1 + E_2$, where the E_1 and E_2 are the kinetic energies of the electrons constituting the pair. Both electrons have to overcome the vacuum barrier given by the work function W_A of the surface. From this it follows that the maximum sum energy E_{sum}^{max} is determined by:

$$E_{\rm sum}^{\rm max} = h\nu - 2W_{\rm A} \ . \tag{2}$$

In the present example the photon energy hv was set to 45 eV and for a Cu(100) surface W_A equals 4.5 eV, hence we obtain $E_{sum}^{max} = 36 \text{ eV}$. In a 2D-Energy distribution lines of constant sum energy are represented by the equation $E_2 = \text{const} - E_1$, which are diagonal lines intercepting the E_1 - and E_2 -axis at an energy value given by the constant. In Fig. 4a) we have added the diagonal line defining E_{sum}^{max} as a solid black line dividing the 2D-Energy window into two parts. We note that in the upper right hand part virtually no intensity is recorded, while in the lower left hand part essentially all intensity is found. This is the consequence of the above discussed energy conservation. This fact demonstrates that we have detected essentially "true" coincidences rather than "random" coincidences. For the latter the maximum sum energy is higher, because we have put the energy of at least two photons into the equation. This result showed that we have successfully moved bevond the mere detection of correlated electron pairs from solid surfaces. We know about the electronic structure of Cu that the 3d-states are energetically about 2-4 eV below the Fermi level, the center of gravity is about 2.5 eV below $E_{\rm F}$. The dashed diagonal line marks the energetic position of pairs, if both electrons come from this average energy level. Since the d-band is completely filled with 10 electrons, whereas the free-electron type sp-band is occupied by approximately 1 electron. We expect the emission from the d-bands to dominate the spectrum. This expectation can be checked, if we use the data shown shown in Fig. 4a) and compute the coincidence intensity as a function of E_{sum} . The result can be seen in Fig. 4b), where the vertical solid lines marks the maximum sum energy as determined by Eq. (2). We see at this point that the coincidence intensity is very low. The finite value is due to the contribution of "random" coincidences. As before, the vertical dashed line

40

30

20

10

0

700

600

500

400

300

200

100

0

0

int. (counts)

0

10

10

20

E₂(eV)





E_{sum} (eV) Figure 4 (online colour at: www.pss-b.com) In panel a) we plot the 2D-Energy distribution of the coincidence intensity in counts obtained from a Cu(100) surface excited with 45 eV photons. The color coding represents the intensity, which is given in counts. The axis are the energies of the individual electron energies. The solid diagonal line indicated the position of the maximum sum energy the pair can have. The dashed diagonal line marks the energetic position of pairs, if both electrons come from the 3dlevels. In panel b) we display the coincidence intensity as a function of the sum energy.

30

40

20

labels the position if the valence band electrons come from the 3d-states with an average binding energy of 2.5 eV. Near this energy position we observe a peak in the spectrum, which tells us that two valence electrons from the dlevels have been emitted. For smaller values of $E_{\rm sum}$ the intensity starts to rise, which is followed by a sudden fall-off for E_{sum} at 15 eV. First, we have to recognize that there is a low kinetic energy cut-off of about 2 eV. Therefore electron pairs with sum energies below 4 eV are not detected. Second, a simple geometric fact tells us that the line of constant sum energy in the 2D-Energy plot becomes shorter if the value of E_{sum} becomes smaller. Within the data shown in Fig. 4a) lies the answer how the energy is shared among the electrons. To make this more apparent it is useful to plot so-called sharing functions. For a given sum energy E_{sum} the coincidence intensity as a function of $E_1 - E_2$ is computed. As an example we show in Fig. 5 the result for $E_{sum} = 35 \pm 1 \text{ eV}$ at a photon energy of 50 eV.



Figure 5 We show the sharing curves for a sum energy $E_{sum} = 35 \pm 1 \text{ eV}$. In panel a) we plot the result obtained from a Cu(100) surface, while the data measured from a Ni(100) surface are shown in panel b). In both cases the photon energy was set to 50 eV. The solid lines serve as guide for the eye.

0 E_1 - $E_2(eV)$ 20

-20

b)

40

With this energy selection we focus on those events, where both electrons come from the vicinity of $E_{\rm F}$. We can clearly observe that for equal energies the intensity is lower than for unequal energies. If we compare the result for both samples, we note that in both cases the sharing function displays a minimum for equal energies of the electron. The minimum can be understood in terms of a selection rule for DPE, which predicts a vanishing DPE intensity if the sum momentum $k_1 + k_2$ is perpendicular to the polarization vector of the light. For the geometry shown in Fig. 3 the polarization is parallel to the surface plane. If the electrons forming a pair have the same kinetic energy and opposite emission angles the sum momentum is along the surface normal and perpendicular to the polarization vector. The difference in the sharing curve can be related to a competing process, which also leads to the emission of electron pairs.

In general two possible pathways for pair emission exist [19, 20]. On one hand, a single photon can be absorbed, which is accompanied by the emission of an electron pair. This is regarded to be a direct double photoemission process (DPE). This process is only possible if the two electrons are correlated [9]. A simple picture illustrating the plausibility of this point is to consider two valence electrons, which initially move independently of each other. Once they collide their motion through the crystal is corre-

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lated. Within the dipole approximation the photon is absorbed by one electron, but by virtue of the electron correlation the second electron is affected as well, which can lead to the emission of a pair. Without correlation between the electrons only single photoemission is possible. This leads us immediately to the other pathway. It is conceivable that the photon is absorbed by a single electron resulting in the creation of a photoelectron. After a series of collisions, in which it looses its initial phase, it may collide with another electron, which creates an electron pair. The process may be called an internal (e,2e) event. The time scale over which these processes take place is of the order of 10 fs. This is beyond the current experimental time resolution of ≈ 1 ns. This issue has been addressed recently by comparing coincidence experiments, where the excitation was via photons or electrons, which will be discussed in detail elsewhere [21]. As far as the data shown in Fig. 5 indicate that in Ni the internal (e,2e) process is more dominant compared to the observation for Cu(100). A theoretical explanation connects these difference to the higher density of states at $E_{\rm F}$ for Ni compared to Cu [20].

3.2 Angular distributions of the double photoemission intensity In the introduction we discussed the concept of the exchange-correlation hole, which is defined in real space. This entity is not accessible via our experiments, because we cannot determine the initial positions of the electrons, which are emitted. What we are able to measure are emission angles and from those it should be in principle possible to deduce the situation in real space. It may be useful at this point to recall the famous Rutherford experiment, where the scattering of α -particles from a thin gold foil was studied. At the time the surprising result was that the *a*-particles experienced also large angular deflections. These could be explained only if the positive nuclear charge was confined into a small region of space. This is an example were angular distributions in scattering experiments reveal the nature of the interaction in real space. Thinking along these lines one should try to access the xchole via the observation of angular distributions of electron pairs. More precisely one should ask the question, how does the angular distribution looks like, if the emission direction of one of the electrons of the pair is fixed. The experimental realization is depicted in Fig. 6. A NaCl(100) surface is excited by a photon beam, which hits the sample under a grazing angle of 12°. The emitted electron pairs travel towards a channelplate detector. The actual detector consists of two parts, namely a central collector and a resistive anode. The central collector accepts electrons only within a a narrow solid angle of ~ 0.02 sr, the detected electron we may term as "fixed electron" in the following. For electrons, which hit the resistive anode the impact position can be determined. Electrons within a solid angle of \approx 1 sr can be detected, which we may term as "free electron". With this instrument we are able to determine the kinetic energies and emission angles of the electrons constituting the pair. Alternatively, we can characterize the co-



Figure 6 (online colour at: www.pss-b.com) Photons hit the surface under a grazing angle of 12° . The emitted electrons hit a channelplate, if their trajectories are within the angular acceptance. The electrons are detected either on a resistive anode or small central collector. Two electrons with momenta k_1 , k_2 and energies E_1 and E_2 are detected in coincidence.

incidence intensity via the momentum of the electrons. More experimental details can found elsewhere [22].

From our previous discussion it is clear that a reasonable starting point to describe the electron-electron interaction is to use a screened Coulomb potential $V \propto (1/r) e^{-r/\lambda}$ acting between the two electrons. The distance between the electrons is given by r, while the screening length is labelled with λ . For crystalline solids the Bloch theorem holds and is therefore adequate to describe the electronic properties in momentum space. In this case the screened Coulomb interaction takes the form $V \propto 1/k^2 + \lambda^{-2}$, where $k = |\mathbf{k}_1 - \mathbf{k}_2|$ is determined by the the momenta of the individual electrons labelled k_1 and k_2 , respectively. From this formula one can derive the following picture. If electrons are well-separated in momentum space, e.g. $|\mathbf{k}_1| = 0$ and \mathbf{k}_2 large compared to the the inverse of the screening length, the interaction is weak and one may consider electrons to be independent. This has the immediate implication that the DPE intensity has to vanish as discussed previously. The other extreme is, if both momenta have the same value the interaction is very strong. The probability to find two electrons in such a state, however, is strongly reduced as a consequence of the xc-hole, which can of course also be introduced in momentum space [23]. As a matter of fact from Eq. (1) one can see immediately that the expression of the pair correlation function xc-hole already connects real space and momentum space, because the pair correlation function depends on the product $r \cdot k_{\rm F}$. The consequence is that the DPE intensity should be very small. In between these two extremes the DPE intensity should have a maximum, since it is more likely to find electrons with slightly different momenta, while the electron-electron interaction is still strong. In summary we derive the following simple picture of the DPE intensity as a function of the

difference momentum k. A minimum of the intensity at k = 0 is followed by a maximum for intermediate values of k, finally at large k values the DPE intensity vanishes. This simple picture is on firm ground, because a dedicated theoretical study of the DPE intensity from a Cu(100) surface reveals exactly this picture. Fominykh et al. [10] find that the emission direction of the fixed electron is surrounded by a reduced intensity of the other electron. This depletion zone is the manifestation of the xc-hole. Since the theoretical study used the components of the in-plane momentum rather than emission angles, we display our experimental study accordingly. Experimentally we chose a NaCl surface to test the prediction of a depletion zone. The energy of the "fixed electron" is labelled with E_1 whereas the "free electron" has the energy E_2 . We observe the onset of DPE when the sum energy $E_1 + E_2$ equals ~14.6 eV if the photon energy is set to 34 eV. This can be easily understood when considering the known binding energies of NaCl determined by photoemission. Wertheim et al. found that the highest occupied level (Cl 3p band) has a binding energy $E_{\rm B} = 9.66 \text{ eV}$ with respect to the vacuum level. Since for DPE two electrons leave the solid this energy needs to be accounted for twice and subtracting this value from the photon energy yields the maximum kinetic sum energy, see Eq. (2). The numerical result is 14.7 eV in agreement with our observation. In the following we want to focus on the momentum distribution rather than the energy distributions. For this we take advantage of the lateral resolution of the set-up. In a first step we select only those coincidences for which the energies E_1 and E_2 are fixed. In order to obtain sufficient statistics we actually select an energy window of ± 0.8 eV around the respective energies. We can now proceed and plot the coincidence intensity as a function of the in-plane momentum k_{\parallel} of the "free electron", see Fig. 7. We would like to point out that all momentum plots display a zero intensity at a position where the central collector is positioned. The position and size of this "blind spot" depends on the momentum of the "free electron". For the plots shown in Fig. 7 this "blind spot" is centered at $k_{\parallel} = 0$ and has a radius of ~0.1 Å⁻¹. In Fig. 7a) the energies are $E_1 = 5.5$ eV and $E_2 = 9.5$ eV. This means we are at the onset of DPE emission. We clearly observe that the region $k_{\parallel} = 0$ (outside the "blind spot") is surrounded by a region of diminished intensity. The intensity increases for larger k_{\parallel} values and reaches a maximum for $k_{\parallel} \approx 0.55 \text{ Å}^{-1}$ and then falls off rapidly at the edge of the channelplate. The reduced intensity around the emission direction of the "fixed" electron will be called the depletion zone in the following. While the theoretical work by Fominykh et al. [10] predicted such a behavior for a Cu(100) surface, we show that this feature also exists for an insulator like NaCl. Because the depletion zone is a manifestation of the xc-hole it is fair to state that the concept of the xc-hole is an experimental reality not just a theoretical concept.

A dramatically different situation is depicted in Fig. 7b) where we select $E_1 = 5.5$ eV and $E_2 = 7.5$ eV. Now the depletion zone is essentially gone. Energetically the



Figure 7 (online colour at: www.pss-b.com) 2D in-plane momentum distribution for two different energy pairs from a NaCl(100). In panel a) we have selected $E_1 = 5.5$ eV and $E_2 = 9.5$ eV. Whereas in panel we have chosen $E_1 = 5.5$ eV and $E_2 = 7.5$ eV, respectively. The color coding represents the intensity, which is given in counts.

sum energy $E_1 + E_2$ has been reduced from 15 eV to 13 eV. Clearly the emergence of the depletion zone is tied to the selection of the energies E_1 and E_2 . We may summarize our observations as follows: (i) if we select the energies E_1 and E_2 such that the sum energy $E_1 + E_2$ has the largest possible value for pair emission the 2D momentum plots display a region of reduced intensity which is centered around the "fixed" electron. (ii) if the sum energy is below the maximum value a more or less uniform momentum distribution is the result.

The experiments using the set-up displayed in Fig. 6 suggested that the angular acceptance is not sufficient to observe the full extension of the depletion zone. Therefore we designed a completely new instrument, which incorporates a large angular acceptance. This results obtained with this set-up will be discussed in the next section.

4 Large angular acceptance set-up The main feature of our new experiment is that it consists of 3 chan-



Figure 8 Sketch of the experimental apparatus and the two geometries used. The linear polarization of the light was in the drawing plane. The *z*-axis of the our coordinate system is perpendicular of the drawing plane of the geometries a) and b). The orientation is of the *y*-axis is along the surface normal of the sample. The emission direction are specified by the angles φ and θ , respectively.

nelplate detectors, which ensure a large angular acceptance, which is in the drawing plane ± 1.57 rad, perpendicular to it ± 0.4 rad is available, see Fig. 8. Delay line anodes allow the determination of the impact positions of electrons even if two electrons hit the same detector. These events we may term as "double hits", whereas we refer to "single hits", if the electrons are registered on different detectors. We operated this instrument in two geometries labelled a) and b) in Fig. 8. For normal incidence of the light the sample masks a large area of one of the detectors. Therefore we operate with only two detectors. In the other geometry the light impinges under an angle of 32° with respect to the normal. We studied a well-ordered Cu(111) surface, which was obtained via Ar sputtering and annealing up to 800 K. The crystallographic $[\overline{2}11]$ direction is in the drawing plane of Fig. 8. The experiments were performed at room temperature. More details of the instrument can be found elsewhere [24]. The photon energy was set to 50 ± 0.2 eV. The polarization plane is in the drawing plane, see Fig. 8. We define a coordinate system, which has the origin at the sample surface, see Fig. 8c). The *y*-axis is always parallel to the surface normal, whereas the *x*- and *z*-direction are in the surface plane and orthogonal to each other. The impact positions are characterized by two angles measured with respect to the surface normal. The angle Θ is in the drawing plane of Fig. 8, while Φ is perpendicular to the drawing plane. Each coincident event is then characterized by 6 coordinates, namely the individual energies and pair of angles Θ and Φ . The total time resolution is approximately 1.4 ns. This will lead to an energy dependent energy resolution, which is 1.5 eV for 20 eV electrons.

It is clear that a six-dimensional presentation of the data is not possible. Therefore one has to reduce the data set such that two-dimensional presentations can be generated. Two possible examples, which demonstrate the capability of the new instrument are: (i) the 2D-energy distribution under a geometrical constraint and (ii) the angular intensity distribution if the emission direction of one electron is fixed.

4.1 Double photoemission at normal photon incidence In our presentation we start with the experimental results obtained with normal incidence of the photons. As described in the experimental part, we use two detectors in this case we may label them "left" and "right", respectively. We further consider only "single" hits, this means only coincidence events where the two electrons hit different detectors are registered. In Fig. 9 we plot the coincidence intensity as a function of the sum energy $E_{\text{sum}} = E_{\text{left}} + E_{\text{right}}$. The vertical dashed line marks the energy position of the maximum sum energy $E_{\text{max}} = 40 \text{ eV}$ imposed by energy conservation, since the work function of the Cu(111) surface ($\approx 5 \text{ eV}$) has to be subtracted twice from the photon energy of 50 eV (see Eq. (2)). It is apparent that the pair emission is governed by a contribution located at $E_{sum} \approx 35$ eV. We recall that the center of gravity of the Cu 3d band is roughly 2.5 eV below the Fermi level



Figure 9 Plot of the E_{sum} distribution of the DPE intensity obtained from a Cu(111) sample. The photon energy is set to 50 eV, the light propagation direction is along the surface normal. The vertical dashed line is the energy position of the highest possible sum energy, which follows from energy conservation. A pronounced emission at 35 eV can be noticed.



Figure 10 Hit pattern of electron pairs is displayed. As axes we use the components of the normalized in-plane momentum of the individual electrons labelled X and Z, respectively. The excitation was via 50 eV photons, which hit the sample along the surface normal. The gray scale on the right displays the intensity in counts. The pair of arcs on the "left" and "right" detector define narrow regions. We will select those events where the "left" and "right" electron come from these regions and compute the energy distributions.

 $E_{\rm F}$, hence we identify the peak at 35 eV with the pair emission from the Cu 3d bands. It is well-known that the Cu(111) surface possesses also a Shockley surface state at the $\overline{\Gamma}$ -point [25]. This state is energetically located in the interval $E_{\rm F}$ and $E_{\rm F} - 0.4$ eV. From Fig. 9 we conclude that with the present apparatus and its current resolution it is not possible to identify the emission from the surface state. The data shown in Fig. 9 is derived from an integration over the whole accessible angular range, even though the shape of the spectrum has a weak angular dependence. The background of the intensity distribution of Fig. 9 and its extension above $E_{\rm sum} = 40$ eV is related to so-called "random" coincidences.

The determination of 2D-energy distributions requires the execution of several steps, therefore we display in Fig. 10 the hit pattern of the individual electrons of coincident pairs as a function of the components of the normalized in-plane momentum (or directional cosine). The directional cosine is labelled X and Z and can be computed from the known emission angles and kinetic energy. One interesting aspect is how the available energy is shared between the electrons, in particular, if we impose geometric constraints. In order to address this point we select regions on the detectors "left" and "right" whose boundaries are given by the pair of arcs in Fig. 10. The width of these regions are 0.15, and the centers have a distance to the origin given by the value of $|\Delta|$. The value chosen for the width is solely determined by statistics. We can now compare the energy distributions for different values of $|\Delta|$. The result is shown in Fig. 11 for a choice of $\Delta = 0.2$ and $\Delta = 0.7$, respectively. Converted into angles, we constrain the mean angle between the trajectories to be either 23° or 89°, respectively. These are the extreme values for the present geometry. The dashed diagonal lines in both plots indicate the position of those events, which have a sum energy of 35 eV. We recall from Fig. 9 that at this energy a prominent pair emission



Figure 11 (online colour at: www.pss-b.com) 2D-energy distributions for $\Delta = 0.2$ in a) and $\Delta = 0.7$ in b). The intensity is given in counts. We added equidistant contours and employed a Gaussian filter. The dashed diagonal line in both plots indicates the emission at $E_{sum} = 35$ eV.

occurs. In Fig. 11 panel a) we observe for $\Delta = 0.2$ a boomerang like distribution. The onset of pair emission at $E_{\text{sum}} = 40 \text{ eV}$ occurs for very unequal energies, which means one of the electrons carries most of the energy. This preference of one electron being "fast" while the other is "slow" also occurs for decreasing sum energy. In general the coincidence intensity increases if $E_{\rm sum}$ decreases. The situation for $\Delta = 0.7$ is different as inspection of Fig. 11b) shows. The onset of pair emission at around $E_{sum} = 40$ eV is not confined to those electrons which have very unequal energies, but occurs for all energy combinations with very similar probability. If we reduce E_{sum} to 35 eV we note that the intensity remains constant as long as the energies are outside the regions 20 eV $<\!E_{\rm left/right}\!<\!30$ eV and $E_{\rm left/right}\!<\!$ 10 eV. From these observations we learn that the prominent emission at $E_{sum} = 35 \text{ eV}$ occurs for unequal energy sharing and preferably for large values of Δ . In other words the trajectories of the electrons have a large angle between each other.

4.2 Depletion zone in the angular distribution We discuss now our results we obtained for the geometry labelled b) in Fig. 8, in this case the light impinges under an angle of 32° with respect to the surface normal. For this we made use of all three detectors, which means we utilized the full angular acceptance of the instrument. Additionally we also considered "double" hits in this experiment. In this case a remark regarding the bookkeeping is necessary. If the two electrons constituting a pair hit different detectors ("single" hits) it is quite natural to label these electrons according to the name given to the detector. If the two electrons hit the same detector ("double" hits) a certain ambiguity arises, since both electrons will have the same label. It is more appropriate to choose a label like "fast" and "slow" with the energies E_{fast} and E_{slow} , respectively. This implies that $E_{\text{fast}} > E_{\text{slow}}$, and in order to compare "single" and "double" hits, we need to use the same labelling for "single" hits, too. After this comment it is warranted to start with the E_{sum} distribution of the coincidence intensity, which we display in Fig. 12. A comparison with Fig. 9, obtained with normal incidence but the same photon energy of 50 eV, shows that the essential features are identical. In both cases we observe the onset of pair emission at about 40 eV, which is dictated by energy conservation, see Eq. (2). A prominent peak at 35 eV can be associated to the emission of 3d valence electrons, as discussed above. The next aspect we want to discuss concerns the 2D-energy distribution, which we show separately for "single" and "double" hits in Fig. 13. The bar on the panel defines the color code for the intensity, which is given in counts. Further, we added equidistant contours to the plot.

In panel a) we plot the distribution for "double hits" and we clearly observe that E_{slow} is confined to values below 10 eV, while it is centered around 5 eV. In contrast to this E_{fast} adopts all values allowed by energy conservation. However, the intensity is not uniform, but we note a steady



Figure 12 Plot of the E_{sum} distribution of the DPE experiment for light incidence of 32° with respect to the normal. The sample is a Cu(111) surface and the photon energy is set to 50 eV. The vertical dashed line is the energy position of the highest possible sum energy, which follows from energy conservation. A pronounced emission at 35 eV can be noticed. This distribution is very similar to the data shown in Fig. 9.



Figure 13 (online colour at: www.pss-b.com) 2D-energy distribution of the DPE intensity from a Cu(111) surface, the photon energy is 50 eV. One electron is termed "fast", whereas the other is called "slow" with energies $E_{\rm fast} > E_{\rm slow}$. In panel a) we show the data for "double" hits, whereas panel b) refers to "single" hits. In both panels we have drawn two circles with radius 1.5 eV. This indicate energy regions centered at $E_{\rm fast} = 23$ eV ($E_{\rm slow} = 12$ eV) and $E_{\rm fast} = 23$ eV ($E_{\rm slow} = 6$ eV). Coincident events within these windows are used for angular distributions of the coincidence intensity, see below.

increase if E_{fast} is below about 20 eV. A comparison of Figs. 13a) and 11a) reveals a strong similarity. This is not surprising if we recall that the definition of "double hits" requires both electrons to hit the same detector. By geometry this inevitably means that the trajectories of the electrons are close to each other. In Fig. 11a) we imposed a similar constraint by selecting a value of $\Delta = 0.2$. Again we state that there is a preference of one electron being "fast" while the other is "slow". In Fig. 13b) we display the 2D-Energy distribution for "single" hits. The first aspect, which we would like to emphasize, is the fact that the intensity is higher compared to "double" hits. This can be read easily from the color bars of the two plots, which shows that the maximum of the 2D-Energy distribution for "single" hits is by a factor of 6 higher than "double" hits. This ratio is also maintained if we compute the total number of these two types of events. From geometry we know that for "single" hits the trajectories of the electrons include a larger angle than those for "double" hits. In other words: the emitted electrons of a pair tend to avoid each other. This aspect will become important later on.

A 2D-angular presentation of our data requires the execution of several steps. First we select values for $E_{\rm fast}$ and $E_{\rm slow}$, respectively. In order to select enough coinci-



Figure 14 (online colour at: www.pss-b.com) Angular distributions with $E_{\text{fast}} = 23 \text{ eV}$ and $E_{\text{slow}} = 12 \text{ eV}$ are displayed. Panel a) shows the 2D angular intensity for the "slow" electron, whereas in panel b) the same for the "fast" electron is plotted. In panel c) we plot the intensity for the "slow" electron if the "fast" electron is constrained to be within the area defined by the black circle of the center detector 2 in b). From panel c) a profile can be computed, which is plotted in panel d). The solid line is guide to eye, whereas the dashed vertical lines mark the boundary of the fixed direction. The intensity is given in counts and the color code is on the right hand side of the plot.

dence events we allow an uncertainty in the energy of ± 1.5 eV. This has been indicated by the circles drawn in Fig. 13. Now we can derive the angular distributions of the "fast" and "slow" electron. These are not independent of each other, since electron pairs are detected. We emphasize that every "fast" electron has a "slow" counterpart. As an example we show in Fig. 14 the angular distributions for "fast" and "slow" electrons centered at $E_{\text{fast}} = 23 \text{ eV}$ and $E_{\text{slow}} = 12 \text{ eV}$ (region a) of Fig. 13. Both distributions display the highest intensity if the electrons leave the sample along the surface normal. The intensity drops for increasing values of $|\Theta|$. The above energy selection for E_{fast} and $E_{\rm slow}$ focusses on the emission from the 3d-states. Contributions from the Shockley surface state were too weak to be identified in our experiments. In the next step we impose a geometrical constraint. We select only those "fast" electrons, which leave the sample within a narrow angular direction. As an example we have drawn a black circle in Fig. 14b), which is centered at $\Theta = \Phi = 0$ rad. The emission direction is a cone with an angle of 0.18 rad, which is the radius of the circle in Fig. 14b). In other words, we fix the direction of the "fast" electron and ask for the intensity

of the "slow" electron around this direction. This is displayed in Fig. 14c) after normalization to the intensity of the "slow" electron in Fig. 14a). This procedure is necessary in order to take into account varying detection efficiencies across the active areas of the detectors. It is obvious that the intensity on the center detector is lower than on the left and right detectors. To emphasize the point and to improve the statistics we integrated the data along the Φ direction and show the resulting profile along the Θ -direction in Fig. 14d). The vertical dashed lines mark the boundary of the allowed Θ values of the "fast" electron. The solid line through the data serves as guide for the eye, the intensity axis is in arbitrary units as a result of our normalization procedure. We applied the same procedure for all profiles. Hence direct comparison is possible. As already evident in Fig. 14c) we observe that the "fast" electron is surrounded by a reduced "slow" electron intensity. We find that the intensity reaches a constant value at a radius $\Theta \sim 1.2$ rad, which is well inside the angular range of our experiment. The key observation is that we are able to show the full extension and shape of the depletion zone. It is of course possible to fix the emission direction of the "slow" electron and determine the intensity map of the "fast" electron. The result of such a presentation is qualitatively and quantitatively identical as far as the size of the depletion zone is concerned. The depletion zone could be observed for different values of E_{fast} and E_{slow} , where the size was independent of the selected energies. We will discuss below under which circumstances, we observe an almost vanishing depletion zone.

If we choose the fixed direction to be centered at $\Theta = 0$ rad the maximum angle of the counterpart cannot exceed 1.57 rad if they are to leave the sample surface. This means the maximum angle between the trajectories is 1.57 rad. However, it is possible to detect electron pairs, whose trajectories include larger angles and to study the angular distribution. This is possible if we explore a significant advantage of our detection scheme. We can select the emission direction of one electron (either "slow" or "fast") anywhere within the angular acceptance. We demonstrate this in Fig. 15. The fixed emission directions are defined by a circle in the 2D angular distribution equivalent to Fig. 14b), which again has a radius of 0.18 rad. The center is either at $\Theta = -1.0$ rad for plots in Fig. 15a) and b), the case $\Theta = 1.0$ rad is depicted in Fig. 15c) and d). The vertical dashed lines in Fig. 15c) and d) mark the range of the allowed Θ values for the fixed electron. With this choice of the emission directions we lose information of the intensity for Θ values on one side of the selected emission direction, but we gain a larger angular range on the other side. In other words: the maximum angle between the trajectories of the fixed "fast" and "slow" electron is larger in this direction. Using the same procedure as before we finally derive the 2D angular distribution of the "slow" electron around the fixed direction of the "fast" electron. These are plotted in Fig. 15a) and c). In the case of panel a) we observe a low intensity on the left detector. If we move



Figure 15 (online colour at: www.pss-b.com) 2D-angular distributions and resulting profiles are shown for electron pairs with $E_{\text{fast}} = 23 \text{ eV}$ and $E_{\text{slow}} = 12 \text{ eV}$. The direction of the fixed "fast" electron is centered either at $\Theta = -1$ rad for panels a) and b) or $\Theta = 1$ rad for panels c) and d). The line profiles of the intensity maps in a) and c) are plotted in panels b) and d). The solid lines are guide to eye, whereas the dashed vertical lines mark the boundaries of the fixed emission directions. The color coding in panels a) and c) represents the intensity, which is given in counts.

to the center detector the intensity has increased and finally the intensity on the right detector is smaller than on the center detector. Again improving the statistics via an integration along the Φ direction is appropriate and gives a more detailed view, the resulting profile can be seen in Fig. 15b). Two important observations can be made. First we see that the intensity peaks at $\Theta \approx 0.2$ rad, while the "fixed" electron is centered at $\Theta \approx -1.0$ rad. This means that the angular size of the depletion zone is ≈ 1.2 rad, in line with the result shown in Fig. 14d). More importantly, we see that the coincidence intensity drops off again if the angle between the two electrons is beyond ≈ 1.2 rad. An equivalent situation is observed in Fig. 15d) despite the breaking of symmetry. We have to emphasize that the photon beam hits the sample with an angle of 32° , see Fig. 8. Therefore we cannot a priori expect to observe a symmetric behavior as we do. We can clearly see that the reduced intensity regime follows the fixed emission direction. The fall-off of the coincidence intensity for large angles between the "fast" and "slow" electron is expected, because

ultimately two electrons are not correlated if they are well separated (in angular or momentum space).

Due to the size of the depletion zone, it is also justified to allow the fixed direction to be rather large. We have found no significant variation of the angular size of the depletion zone for other values of $E_{\rm fast}$ and $E_{\rm slow}$. This means that in momentum space the depletion zone size will scale with the square root of the energy.

We would like to come back to the 2D-Energy distribution shown in Fig. 13. We have pointed out before that most of the coincidence intensity occurs for $E_{\text{slow}} < 10 \text{ eV}$. This preference was mainly due to "double" hits. Detection on the same detector implicitly means that the trajectories of the electrons include small angles, hence they are "close" to each other. If we select the energies centered at $E_{\text{fast}} = 23 \text{ eV}$ and $E_{\text{slow}} = 6 \text{ eV}$ (region b) of Fig. 13, we are focussing on such events and ask how the angular distributions are affected. The result for the "slow" electron around the fixed direction of the "fast" electron is plotted in Fig. 16. We observe that the depletion zone has been "filled" and an almost constant intensity as a function of Θ is observed. This filling of the depletion zone occurs gradually if we vary E_{slow} from 12 eV to 6 eV. More specifically the size of the depletion zone stays essentially constant, but the minimum is filled up. A simple picture of the electron-electron scattering, where the interaction between the electrons is mediated by the Coulomb interaction, shows that if the trajectories are forced to be close to each other one electron is "fast" while the other is "slow". In general two electrons tend to avoid each other (due to the Pauli principle and Coulomb interaction) leading to the concept of the depletion zone. Our experiments confirm this picture as long as the individual energies E_{fast} and E_{slow} are not too unequal as just shown.



Figure 16 Coincidence intensity for the "slow" electron if the direction of the "fast" electron is fixed at $\Theta = 0$ rad. We selected $E_{\text{fast}} = 23 \text{ eV}$ and $E_{\text{slow}} = 6 \text{ eV}$. The solid line is guide to eye, whereas the dashed vertical lines mark the boundary of the fixed direction.

We conclude that we are able to fully map the depletion zone. This statement constitutes the major achievement of this work. We find for the depletion zone from electrons originating from a Cu(111) surface a size of ≈ 1.2 rad independent of the energy of the electrons. We also discovered a correlation in energy space proven by an almost disappearing depletion zone if the electron energies are very unequal. It would be desirable to compare our experimental depletion zone size with theory. This is, however, beyond the capability of current solid state theory. Eventually, the comparison of theory and experiment of the depletion zone may lead to an improved description of the exchange-correlation hole in solids.

5 Summary We have outlined the development of double photoemission from solid surfaces over recent years. The relevance of this technique rests on the fact that for independent electrons the DPE intensity vanishes. Therefore DPE experiments are particularly suited to study the electron-electron interaction. This in turn holds the promise that these experiments help to develop a theory beyond the effective independent electron description. We established that energy and angular distributions can be obtained, the latter over a large angular acceptance. The sum energy distributions reveal that the onset of the coincidence intensity occurs at an energy, which is determined by the photon energy and the work function of the sample. We learn further that the available energy is in general unequally shared. The angular distributions of the DPE intensity prove that the exchange-correlation hole is an experimental reality. It manifests itself in a depletion zone of the coincidence intensity around the fixed emission direction of one electron. It is a challenge for theory to determine from our angular distributions the exchange-correlation hole in real space.

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References

- [1] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).
- [2] H. Ibach and H. Lüth, Solid-State Physics (Springer-Verlag, Berlin, 1991).

- [3] J. C. Slater, Rev. Mod. Phys. 6, 209 (1934).
- [4] N. F. Mott and H. Jones, The Theory of the properties of metals and alloys (Oxford University Press, Oxford, 1936)
- [5] M. Nekovee, W. M. C. Foulkes, and R. J. Needs, Phys. Rev. B 68, 235108 (2003).
- [6] L. A. Constantin, J. P. Perdew, and J. Tao, Phys. Rev. B 73, 205104 (2006).
- [7] A. Puzder, M. Y. Chou, and R. Q. Hood, Phys. Rev. A 64, 022501 (2001).
- [8] K. Byczuk, M. Kollar, K. Held, Y.-F. Yang, I. A. Nekrasov, T. Pruschke, and D. Vollhardt, Nature Phys. 3, 168 (2007) and references therein.
- [9] J. Berakdar, Phys. Rev. B 58, 9808 (1998).
- [10] N. Fominykh, J. Berakdar, J. Henk, and P. Bruno, Phys. Rev. Lett. 89, 086402 (2002).
- N. Fominykh, J. Henk, J. Berakdar, P. Bruno, H. Gollisch, [11] and R. Feder, Solid State Commun. 113, 665 (2000).
- [12] H. Gollisch, N. v. Schwartzenberg, and R. Feder, Phys. Rev. B 74, 075407 (2006).
- [13] P. Lablanquie, J. H. D. Eland, I. Nenner, P. Morin, J. Delwiche, and M.-J. Hubin-Franskin, Phys. Rev. Lett. 58, 992 (1987).
- [14] J. Mazeau, P. Selles, D. Waymel, and A. Huetz, Phys. Rev. Lett. 67, 820 (1991).
- [15] O. Schwarzkopf, B. Krässig, J. Elmiger, and V. Schmidt, Phys. Rev. Lett. 70, 3008 (1993).
- [16] C. Gazier and J. R. Prescott, Phys. Lett. A 32, 425 (1970).
- [17] H. W. Biester, M. J. Besnard, G. Dujardin, L. Hellner, and E. E. Koch, Phys. Rev. Lett. 59, 1277 (1987).
- [18] H. W. Biester, M. J. Besnard, G. Dujardin, L. Hellner, and E. E. Koch, Phys. Rev. Lett. 60, 1589 (1988).
- [19] R. Herrmann, S. Samarin, H. Schwabe, and J. Kirschner, Phys. Rev. Lett. 81, 2148 (1998).
- [20] N. Fominykh, J. Berakdar, J. Henk, S. Samarin, A. Morozov, F. U. Hillebrecht, J. Kirscher, and P. Bruno, in: Solid-State Photoemission and Related Methods: Theory and Experiment, edited by W. Schattke and M. A. van Hove (Wiley-VCH Verlag, Weinheim, 2003) Chap. 10.
- [21] M. Munoz-Navia, C. Winkler, R. Patel, M. Birke, F. O. Schumann, and J. Kirscher (to be published).
- [22] F. O. Schumann, C. Winkler, G. Kerherve, and J. Kirschner, Phys. Rev. B 73, 041404(R) (2006).
- [23] P. Fulde, Electron Correlations in Molecules and Solids, Springer Series in Solid-State Sciences Vol. 100 (Springer, Berlin, 1991).
- [24] F. O. Schumann, C. Winkler, and J. Kirschner, New J. Phys. 9, 372 (2007).
- [25] S. G. Louie, P. Thiry, R. Pinchaux, Y. Pettroff, D. Chandesris, and J. Lecante, Phys. Rev. Lett. 44, 549 (1980).