Spectroscopy of electron correlations in superconductors

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The one-photon two-electron emission process is suggested as a spectroscopic tool for studying the features of Cooper pairs in superconducting materials with a pairing mechanism. It is shown that the correlated angle distributions of the photo-excited electron pair carry detailed information on the Cooper pair wave function in the momentum space. Utilising circularly polarised photons offers the possibility of investigating aspects pertinent to the phase of the superconducting gap function. Phase information are accessed via measuring the circular dichroism in the two-electron angular and energy distribution, i.e. the difference in the recorded two-electron photoemission spectra for left and right circularly polarised photon.

1. Introduction

A variety of experimental tools have been utilized for studying the properties of superconductive materials. Of particular interest are the magnitude, the symmetry and the temperature dependence of the superconducting gap. These aspects have been addressed by a number of methods, most notably neutron and polarization-resolved Raman spectroscopy [1, 2], infrared photoabsorption spectroscopy [3], de Haas-van Alphen effect [4], and scanning tunnelling spectroscopy [5–7]. A particularly powerful technique is the photoemission spectroscopy (PES) [8–10] in which following the irradiation of the material by monochromatic photons, the emitted electrons are detected and their emission angles and energies are resolved. In PES only one photoelectron is detected. Hence, a direct study of the two-particle correlation is not possible with this technique, even though these correlations may show up as subsidiary structures in the single particle spectra. Recently we developed the first theory [11] for the two-electron photoemission (DPE) from superconducting (SC) materials. In DPE an electron pair is emitted from a sample upon absorbing one ultraviolet photon. The correlation within the pair is mapped out by fixing the wave vector of one of the detected electrons while scanning the wave vector of the other [12, 13]. On the basis of the BCS theory [14] for conventional superconductors it turned out that, under specific conditions that

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are realizable in a DPE experiment, a Cooper pair in a SC sample can be excited by one vacuum ultra violet photon [1]. The spectra of the excited electron pair carry direct information on the energy and the angular pair correlation. In particular, the condensation of Cooper pairs in the two-electron state with a zero total momentum produces characteristic peaks in the two-particle energy and angular (momentum-space) correlation functions. These findings establish the unique potential of DPE for investigating the two-particle properties of the Cooper pair states and hence shed new light on mechanisms driving superconductivity in diverse SC materials; in particular we expect DPE to be instrumental in understanding the details of two-particle correlation in high-temperature SC (HTSC) compounds [15].

In this work we extend our theory on the electron pair emission from SC materials to include the case of circularly polarized photons. As shown below the utilization of polarized photons gives access to information on the phase of the gap function and allows studying the phase dependence on the inter-particle correlation. Specifically, employing the plane-wave approximation for the treatment of the vacuum electron pair states we show that the momentum space wave function of the Cooper pair can be studied in detail using the DPE method. Firstly, the density of the Cooper pair state in the relative-momentum space can be mapped through measuring the correlated angle distribution of electrons within the excited electron pair. This allows for investigation of the symmetry of SC gap. Secondly, the circular dichrosim, i.e. the measured difference in the DPE probability between left and right polarized light, is directly related to the phase of the Cooper pair wave function in the relative-momentum space. This remarkable feature is of particular importance for studying those SC materials that exhibit a time-symmetry breaking superconductivity [10].

The paper is organized as follows. In section 1 we develop a general theory for the rate of the DPE process in the case of circularly polarized photons. The plane wave approximation for the photoelectron pair is specified. The expression for circular dichroic effect is also derived. In section 2 we apply the developed theory to the case of one-photon Cooper pair emission from SC sample. Then in section 3 we inspect some particular situations, where the density and the phase of Cooper pair state in the relative-momentum space is studied using DPE method. Conclusions are made in section 4 and atomic units (a.u.) $\hbar = e = m_e = 1$ are used throughout.

2. General theory

Consider the emission of an electron pair from a clean sample into the vacuum following the absorption of a single circularly polarized vacuum ultra violet photon. The cross section of this DPE process is given by

$$\Gamma_{\mathbf{e}} \propto \sum_i \left| \langle \Psi_{p_1, p_2} | D_{12} | \Phi_i \rangle \right|^2 \delta(E_1 + E_2 - E_i - \omega), \tag{1}$$

where the asymptotic photoelectron momenta and spins are specified by p_1 and p_2 ($p_j \equiv \mathbf{p}_j \sigma_j$, $j = 1,2$), respectively, $\Psi_{p_1, p_2} (\Phi_i)$ is the final (initial) two-electron state with

energy $E_1 + E_2$ (E_i), ω is the photon frequency. The coupling of the electron pair to the photon field is described by the operator D_{12} as follows:

$$D_{12} = -i[\exp(iqr_1)(e \cdot \nabla_1) + \exp(iqr_2)(e \cdot \nabla_2)], \tag{2}$$

where $e = e_{x'} + ie_{y'}$ is the polarization vector and q is the wave vector [$(e_{x'/y'} \cdot q) = 0$] in the case of a right-hand circularly polarized photon. The case of a left-hand circularly polarized photon derives from (2) upon performing the complex conjugate $e \to e^*$.

Operating within the Jacobi coordinates, i.e. transforming to the centre-of-mass coordinate $R = (r_1 + r_2)/2$ and the relative coordinate $r = r_1 - r_2$ we can rewrite (2) as

$$D_{12} = -i\exp(iqR)\left[\cos\left(\frac{qr}{2}\right)(e \cdot \nabla_R) + 2i\sin\left(\frac{qr}{2}\right)(e \cdot \nabla_r)\right]. \tag{3}$$

Note that in the dipole approximation ($q = 0$) the operator D_{12} acts only on the centre-of-mass coordinate R of the electron pair, i.e. the photon field influences only the centre-of-mass motion of electrons and it does not affect their relative motion. Here we include in our considerations non-dipolar terms, i.e. we use D_{12}, as given by equation (3), for the photon-electron coupling.

Now we evaluate the matrix element

$$M_e = \langle \Psi_{p_1, p_2} | D_{12} | \Phi_i \rangle. \tag{4}$$

Here we omitted for the sake of brevity the spin indices, because the operator D_{12} [see equations (2) and (3)] does not depend on the electron spin variables. Thus, the final and the initial spin states of the electron pair are the same. Using (3) we obtain

$$M_e = e \cdot \int dQ \int dk \Psi_{P,p}^*(Q, k)$$
$$\times \left[\left(\frac{Q}{2} + k\right)\Phi_i\left(Q - q, k - \frac{q}{2}\right) + \left(\frac{Q}{2} - k\right)\Phi_i\left(Q - q, k + \frac{q}{2}\right)\right], \tag{5}$$

where $P = p_1 + p_2$ and $p = (p_1 - p_2)/2$ are respectively the total and relative momentum of electron pair. In the plane wave approximation the relation applies

$$\Psi_{P,p}(Q, k) = \delta^{(3)}(P - Q)\delta^{(3)}(p - q). \tag{6}$$

Hence the matrix elements read

$$M_e = e \cdot \left[\left(\frac{P}{2} + p\right)\Phi_i\left(P - q, p - \frac{q}{2}\right) + \left(\frac{P}{2} - p\right)\Phi_i\left(P - q, p + \frac{q}{2}\right)\right]$$
$$\cong (e \cdot P)\Phi_i(P - q, p) - (e \cdot p)(q \cdot \nabla_p\Phi_i(P - q, p)), \tag{7}$$

in deriving this relation we retained only linear terms in $|q|/|p|$ since $|q| \ll |p|$. We note that the value of the inter-particle momentum $|p|$ is chosen by the experiment and is usually large, for in the case $|p| \to 0$ the two-particle density vanishes due to exchange and correlation and hence the DPE cross section diminishes. The plane wave approximation is justified in situations where the electrons have high energies (compared to the Fermi energy) and screening in the sample is substantial. Such situations are encountered in the case of ultraviolet photons and metallic and/or SC targets [16].

To elucidate how information on the phase of the Cooper pair wave function can be accessed we write the initial two-particle state in the form $\Phi_i = |\Phi_i|\exp(i\Phi_i)$.

The matrix elements attain then the form

$$M_e = \exp[i\varphi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})][(\boldsymbol{e} \cdot \boldsymbol{P})|\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})| - (\boldsymbol{e} \cdot \boldsymbol{p})(\boldsymbol{q} \cdot \nabla_p |\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})|) \\ - i(\boldsymbol{e} \cdot \boldsymbol{p})|\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})|(\boldsymbol{q} \cdot \nabla_p \varphi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p}))]. \tag{8}$$

Inserting this expression in (1) and neglecting higher-order terms with respect to q, we deduce for the probability of DPE process that

$$\Gamma_e \propto |(\boldsymbol{e} \cdot \boldsymbol{P})|^2 \sum_i |\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})|^2 \delta(E_1 + E_2 - E_i - \omega). \tag{9}$$

The DPE rate is thus directly proportional to the two-electron spectral function in the momentum space representation

$$A_{12}(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p}; E_1 + E_2 - \omega) = \sum_i |\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})|^2 \delta(E_1 + E_2 - E_i - \omega). \tag{10}$$

Now we define the (normalized) circular dichroism as the (relative) difference in the DPE cross sections corresponding to the absorption of right-hand and left-hand circularly polarized photons, i.e.

$$CD = \frac{\sum_i \left(|M_e|^2 - |M_{e^*}|^2\right) \delta(E_1 + E_2 - E_i - \omega)}{\sum_i \left(|M_e|^2 + |M_{e^*}|^2\right) \delta(E_1 + E_2 - E_i - \omega)}. \tag{11}$$

Using (1) and (8), we derive for the circular dichroism

$$CD = \frac{2\text{Im}[(\boldsymbol{e} \cdot \boldsymbol{p})(\boldsymbol{e}^* \cdot \boldsymbol{P})]}{|(\boldsymbol{e} \cdot \boldsymbol{P})|^2} \frac{\sum_i |\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})|^2 (\boldsymbol{q} \cdot \nabla_p \varphi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})) \delta(E_1 + E_2 - E_i - \omega)}{\sum_i |\Phi_i(\boldsymbol{P} - \boldsymbol{q}, \boldsymbol{p})|^2 \delta(E_1 + E_2 - E_i - \omega)}. \tag{12}$$

Here we retained in the denominator only the zero-order terms with respect to q. The key feature of the result (11, 12) is that the circular dichroism vanishes if the phase of the two-electron wave function is a uniform function of the relative electron momentum $\boldsymbol{p}$. We exploit this fact below when considering the DPE from the Cooper pair state in a SC sample.

3. DPE from Cooper pair state

Let us consider the DPE process from a SC sample with a clean flat surface. We assume the target material to possess a two-dimensional electronic structure with the (super)conducting planes being parallel to the surface. Equation (9) reduces then to [the vector components parallel (perpendicular) to the surface are labelled with ($\perp$)]

$$\Gamma_e^{CP} = P_\perp^2 |e_\perp|^2 |\Phi_{CP}(P_\perp - q_\perp, \boldsymbol{p}_\parallel)|^2 \delta^{(2)}(\boldsymbol{P}_\parallel - \boldsymbol{q}_\parallel) \delta(E_1 + E_2 - E_{CP} - \omega), \tag{13}$$

where we took into account that, due to condensation, all the Cooper pairs are in the same two-electron state ($i \equiv CP$) with a well-defined energy E_{CP} as well as a zero total wave vector parallel to the surface. This fact is reflected in the appearance of the delta-function $\delta^{(2)}(\boldsymbol{P}_\parallel - \boldsymbol{q}_\parallel)$ in equation (13). As inferred from (12) the DPE probability is determined by the momentum-space density of the Cooper pair in

the $|\Phi_{CP}|^2$. This quantity can therefore be mapped out in a DPE experiment by scanning the electron momenta of the two emitted correlated photoelectrons under the following conditions: $\boldsymbol{P}_\| = \boldsymbol{q}_\|$ and $E_1 + E_2 = E_{CP} + \omega$.

Using the BCS model [14], for the wave function of Cooper pair Φ_{CP} we conclude that

$$\Phi_{CP}(P_\perp - q_\perp, \boldsymbol{p}_\|) = \frac{f(P_\perp - q_\perp)\Delta_{p_\|}}{2E_{p_\|}}, \quad E_{p_\|} = \left(\varepsilon_{p_\|}^2 + \left|\Delta_{p\|}\right|^2\right)^{1/2}. \tag{14}$$

Here $\Delta_{p_\|}$ is the SC gap function and $\varepsilon_{p_\|}$ is the energy of the elementary excitations in the normal (metallic) state. The factor $f(P_\perp - q_\perp)$ accounts for violation of the Cooper pair total momentum perpendicular to the surface. Inserting (13) in (12) we obtain

$$\Gamma_e^{CP} = P_\perp^2 |e_\perp f(P_\perp - q_\perp)|^2 \frac{|\Delta_{p_\|}|^2}{4\left(\varepsilon_{p_\|}^2 + |\Delta_{p_\|}|^2\right)} \delta^{(2)}(\boldsymbol{P}_\| - \boldsymbol{q}_\|)\delta(E_1 + E_2 - E_{CP} - \omega). \tag{15}$$

Inspecting the structure of this equation we note that the momentum dependence of the absolute square of the gap function $|\Delta_{p_\|}|^2$ and, in particular, its nodes can be determined by the DPE experiment. This can be done by scanning the relative momentum of the electron pair parallel to the surface $\boldsymbol{p}_\|$ amounting to the measurement of the correlated angular distribution of emitted photoelectrons under the kinematics: $\boldsymbol{P}_\| = \boldsymbol{q}_\|$ and $E_1 + E_2 = E_{CP} + \omega$. It should be noted that the absolute value of the SC gap $|\Delta_{p_\|}|$ can be also determined using angle-resolved single-electron photoemission [17]. However in the latter case, one should compare the angle-resolved photoelectron spectra in the normal and SC states, respectively, in order to infer $|\Delta_{p_\|}|$. In addition, in contrast to DPE, in SPE no information can be inferred on the dependence of the phase on the inter-particle correlation.

Now we consider the circular dichroism in the case of DPE from the Cooper pair state. Equation (11) reduces to

$$CD(CP) = K(e; P_\perp, \boldsymbol{p}_\|)\big(\boldsymbol{q}_\| \cdot \nabla_{p_\|} \varphi_{CP}(\boldsymbol{p}_\|)\big), \tag{16}$$

where

$$K(e; P_\perp, \boldsymbol{p}_\|) = \frac{2\text{Im}[(\boldsymbol{e}_\| \cdot \boldsymbol{p}_\|)e_\perp^*]}{P_\perp^2 |e_\perp|^2} \tag{17}$$

is a geometrical (kinematical) factor. Note that the dependence of the phase Φ_{CP} on the total pair momentum should be taken into account if there are SC currents in the sample. Here we suppose that no voltage nor magnetic fields are applied to the sample so that no (steady) current is present.

Presenting the SC gap function in the form $\Delta = |\Delta|\exp(i\chi)$ and using (13), we obtain in accordance with (15) that

$$CD(CP) = K(e; P_\perp, \boldsymbol{p}_\|)\big(\boldsymbol{q}_\| \cdot \nabla_{p_\|} \chi_{p_\|}\big). \tag{18}$$

It is clear from this equation that $CD(CP)$ vanishes if the phase of SC gap function is a uniform function of the relative pair momentum. This is, for example, the case of conventional *s*-wave superconductors. In the DPE experiment the mapping of the circular dichroic effect (17) can be realised through the measurements of the

correlated angular distributions of the electrons in the kinematical regime: $P_\parallel = q_\parallel$ and $E_1 + E_2 = E_{CP} + \omega$. Regarding equation (17) it is also important to note that it holds true only if $|\Delta_{p_\parallel}| \neq 0$, otherwise $CD(CP) = 0$.

4. Examples

In order to illustrate the theory developed above with concrete examples, we consider a situation which is of relevance to copper oxide HTSC materials. Namely, we consider the case of the $d_{x^2-y^2}$-wave pairing symmetry in CuO_2 planes [18]

$$\Delta_k = \Delta_{x^2-y^2}[\cos(k_x a) - \cos(k_y a)], \tag{19}$$

where a stands for the lattice constant. We suppose that in the DPE set-up the CuO_2 planes are parallel to the surface. Such a geometry is usually utilized in the experimental set-ups of angle-resolved single-electron photoemission studies on HTSC materials [17]. It can be deduced from (14) that in the case of $d_{x^2-y^2}$-wave pairing [18] the corresponding DPE cross section vanishes if $p_x = \pm p_y$. This observation provides a test for the symmetry of the SC gap in a DPE experiment.

Since the SC gap (18) is a real function the circular dichroism is identically zero in this case. However, the admixture of s-wave pairing symmetry [19, 20]

$$\Delta_k = \Delta_{x^2-y^2}[\cos(k_x a) - \cos(k_y a)] + i\Delta_s \tag{20}$$

induces a circular dichroic effect in the correlated angular electron-pair distributions. Indeed, using (19) in equation (17) we derive

$$CD(CP) = K(e; P_\perp, p_\parallel) \frac{\Delta_{x^2-y^2}\Delta_s[aq_x \sin(p_x a) - aq_y \sin(p_y a)]}{\Delta_{x^2-y^2}^2[\cos(p_x a) - \cos(p_y a)]^2 + \Delta_s^2}. \tag{21}$$

It is seen that the circular dichroism is measured by scanning the relative momentum of emitted electron pair or by changing the photon impact direction. In particular, for the photon geometry $q_x = q_y$ one has $CD(CP) = 0$ in the kinematical regime $p_x = p_y$. This corresponds to a vanishing DPE cross section in the case of a pure $d_{x^2-y^2}$-wave pairing symmetry [18]. However, this situation changes, for example, for the photon geometry $q_x \neq 0$, $q_y = 0$.

For comparison we consider another possible scenario: the $d_{x^2-y^2}$-wave pairing symmetry with admixture of d_{xy}-wave component [20, 21]

$$\Delta_k = \Delta_{x^2-y^2}[\cos(k_x a) - \cos(k_y a)] + i\Delta_{xy} \sin(k_x a) \sin(k_y a). \tag{22}$$

The corresponding result for the circular dichroism is given by

$$CD(CP) = K(e; P_\perp, p_\parallel) \frac{\Delta_{x^2-y^2}\Delta_{xy}[aq_x \sin(p_y a) - aq_y \sin(p_x a)][1 - \cos(p_x a)\cos(p_y a)]}{\Delta_{x^2-y^2}^2[\cos(p_x a) - \cos(p_y a)]^2 + \Delta_{xy}^2[\sin(p_x a)\sin(p_y a)]^2}.$$

$$\tag{23}$$

This expression is more involved than (21), however the dependence of the circular dichroism on the photon geometry is similar to that of (21).

The SC gap functions (19), (20), and (22) correspond to the singlet pairing. In the case of the $d_{x^2-y^2} + i(p_x \pm p_y)$ superconductor [20] one has the singlet pairing component with an admixture of the triplet pairing component. For studying this exotic case using the DPE method, one should utilize in addition to the circular dichroism measurements the spin-resolved measurements, for the spin state of the emitted pair is the same as that of Cooper pair.

5. Summary and conclusions

In summary, we have considered theoretically the emission into the vacuum of correlated electron pairs from a solid sample following the absorption of one circularly polarized photon. Expressions for the DPE probabilities and for the circular dichroism have been derived using the plane wave approximation for the vacuum-state electrons. Using the BCS theory in the case of SC materials with two-dimensional electronic structure, we were able to relate the DPE cross sections and the circular dichroism to respectively the absolute value and the phase of the SC gap function. The different pairing symmetries, which can be of relevance to the HTSC materials, have been considered and their characteristic effects on the correlated DPE angular distributions have been determined.

The results of our present analysis show that using the DPE method allows mapping the absolute value of the SC gap function in the momentum space. The phase of the SC gap function can be studied by means of the DPE technique via measuring the circular dichroism in the correlated electron-pair angular distributions. We expect that the findings of the present study are most relevant to DPE from HTSC materials, in which case the symmetry of the SC gap function is still under discussion and the SC mechanisms are still to be established.

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