

Polarisation, Spin and Time in Photoemission

How to calculate the photoelectron spin density matrix from the polarisation tensor of the light: V2.2

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Abstract

These notes describe a general photoemission process from the semi-classical viewpoint: under the influence of an external electromagnetic field, a photoelectron is excited and detected externally. Using the evolution operator, the time-dependence of the field can be described – pulsed excitations and so on – and there is no restriction to Golden-Rule-type steady state situations. The detection process involves a measurement of the energy, propagation direction and spin of the photoelectron, and is encapsulated in a set of suitably defined operators. The polarisation state of the electromagnetic field is described by the classical polarisation tensor and the spin state of the photoelectron is compactly described by its spin density matrix.

The central result of this analysis is the identification of a “transition probability matrix” which determines the spectral weight of all possible light-excited electronic transitions. The experimental parameters of the particular measurement performed determine which components of the transition probability matrix contribute to the spectrum. These notes show how this works in general, and give examples of spin-polarisation and dichroism in photoemission. The special role of spin-orbit coupling in the electron states is noted.

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1 Pre-amble

The motivation for this formulation of the calculation of photoemission spectra comes from the many experimental developments that have been made since the original angle-resolved measurements. These include

- electron spin-resolution;
- exploitation of photon polarisation to observe various types of dichroism;
- the potential use of sub-femtosecond (even attosecond) pulses in pump-probe experiments to observe the evolution or dynamical response of electron systems directly in the time domain.

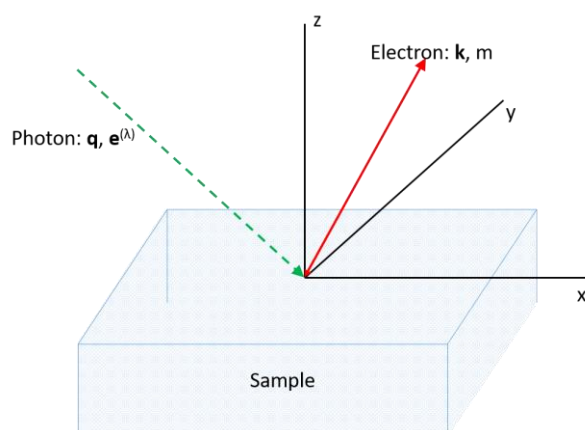
These notes show how to incorporate these aspects into photoemission calculations at the 1-electron level.

In this semi-classical version of the formulation, the electromagnetic field is treated as a classical time-dependent external field acting on the electrons. It is not hard to modify the formulation to include a fully quantised photon field, and this may become an interesting point in condensed matter physics as (free-electron) laser excitation becomes more available.

A further key point is that this formulation is a 1-electron theory; the interaction between electrons is smuggled into an effective self-consistent field potential via some approximation such as density functional theory. Sometimes many-electron excitation effects are included phenomenologically by means of a complex self-energy (or simply by using solutions of the 1-electron Schrödinger equation for complex energies). At all events, our approach here is to treat the electrons as moving independently in an effective 1-electron potential. Experience shows that this is a surprisingly accurate and physically illuminating thing to do.

2 The geometry of the system

We consider an electron system (atom, molecule, crystal) in an external electromagnetic field whose polarisation state will be specified by classical polarisation tensor involving the Stokes Parameters – see section 4. We use a set of Cartesian axes (plus the related polar coordinates) to describe electron positions – this set is arbitrary but for an atom in a crystal we'd take them to be the natural crystal-fixed axes. The direction of the incident photon and its polarisation basis unit vectors $\mathbf{e}^{(\lambda)}$ are also given with respect to these Cartesian axes. Since this is a photoemission problem, we'll take the crystal to occupy the $z < 0$ half-space; the positive z -axis is therefore the outward-pointing surface normal.



3 Basics

3.1 Hamiltonian

The Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}(t) \quad (3.1)$$

Here \mathcal{H}_0 is the non-interacting Hamiltonian and $\mathcal{V}(t)$ is the electron-field interaction.

The Electronic Hamiltonian

The non-interacting Hamiltonian for the electron is

$$\mathcal{H}_0 = \sum_i E_i |\psi_i\rangle \langle \psi_i| \quad (3.2)$$

where ψ_i is a composite symbol describing all the electron orbital/spatial and spin degrees of freedom of the electron. Let's be more precise about this. Clearly $|\psi_i\rangle$ is an energy eigenket corresponding to energy eigenvalue E_i , which may be degenerate. Moreover, the spectrum of energy eigenvalues will in general have a discrete part, at low energies, corresponding to the bound states of the system, and a continuous part, above a certain energy threshold, corresponding to the unbound states. These unbound states can be naturally represented as scattering states – solutions of the Lipmann-Schwinger equation [1] – and they are (partly) characterised by a continuous energy variable. In this situation it's useful to invent a good notation with which to expand the “composite” index i in (3.2).

For example, if the system is an atom without spin-orbit coupling the spherical symmetry suggests using a complete set of commuting observables - CSCO [1], [2] consisting of the Hamiltonian, the orbital angular momentum l (actually l^2), its z-component l_z , the electron spin angular momentum s and the z-component of the spin s_z . The natural labelling of the bound state energy eigenkets is thus

$$\begin{aligned} |\psi_i\rangle &\rightarrow |n, l, m_l, m_s\rangle \\ E_i &\rightarrow E_{n, l, m_l, m_s} \end{aligned} \quad (3.3)$$

Here, as we know, n is the so-called principal quantum number (equal to 1 + the number of nodes in the radial wave function), and l, m_s, m_s are the eigenvalues of l, l_z, s_z respectively¹. The spherical symmetry of the atomic potential ensures that the energy eigenvalue does not depend on m_l or m_s and is therefore $2(2l+1)$ -fold degenerate (the first factor of 2 corresponding to spin). Similarly, the natural labelling of the continuum states is

$$\begin{aligned} |\psi_i\rangle &\rightarrow |\varepsilon, l, m_l, m_s\rangle \\ E_i &\rightarrow \varepsilon \end{aligned} \quad (3.4)$$

¹ No need to specify the eigenvalue of s ; it's always $\frac{1}{2}$.

In the presence of spin-orbit coupling, l, m_l, m_s have to be replaced in this labelling scheme by j and m_j (the eigenvalues of j and j_z respectively) where $j = l + s$. We'll return to this point in section 3.2.

For systems which are molecules, clusters, solids etc. the symmetries, if any, and therefore the natural components of the CSCO, are obviously more complicated, but the principles are the same. So let's introduce the following general notation.

$$\begin{aligned} \text{Bound states: } \quad \mathcal{H}_0 |n, Q\rangle &= E_{n,Q} |n, Q\rangle & E_{n,Q} < 0 \\ \text{Continuum states: } \quad \mathcal{H}_0 |\varepsilon, Q\rangle &= \varepsilon |\varepsilon, Q\rangle & \varepsilon \geq 0 \end{aligned} \quad (3.5)$$

Here we have used the composite index Q to represent all parts of the CSCO other than the Hamiltonian – for an atom $Q \rightarrow l, m_l, m_s$, and so on. We also took the zero of energy to be the continuum threshold.

This set of eigenkets has the following properties:

Orthonormality:

$$\begin{aligned} \langle n, Q | n', Q' \rangle &= \delta_{nn'} \delta_{QQ'} \\ \langle n, Q | \varepsilon, Q' \rangle &= 0 \\ \langle \varepsilon, Q | \varepsilon', Q' \rangle &= \delta(\varepsilon - \varepsilon') \delta_{QQ'} \end{aligned} \quad (3.6)$$

Completeness:

$$\sum_Q \left(\sum_n |n, Q\rangle \langle n, Q| + \int_0^\infty d\varepsilon |\varepsilon, Q\rangle \langle \varepsilon, Q| \right) \quad (3.7)$$

The Interaction with the Field

In this section, all the interactions are given in the Schrödinger picture, denoted [S]. In the dipole approximation, we can write the electron-field interaction in the form [2], [3]

$$\mathcal{V}^{[S]}(t) = \mathcal{V}^{(x)}(\mathbf{q}, t) = -e\mathbf{E}^{(x)}(\mathbf{q}, t) \cdot \mathbf{r} = \mathbf{E}^{(x)}(\mathbf{q}, t) \cdot \mathbf{d} \quad (3.8)$$

Here \mathbf{r} is the electron position operator, the dipole operator is simply $\mathbf{d} = -e\mathbf{r}$, and $\mathbf{E}^{(x)}(\mathbf{q}, t)$ is the electric field corresponding to a wave propagating with wave-vector \mathbf{q} in a general polarisation state denoted by a unit vector $\mathbf{e}^{(x)}(\mathbf{q})$. We can express this as a linear combination of the polarisation basis vectors $\mathbf{e}^{(\lambda)}(\mathbf{q})$ defined in Appendix A

$$\begin{aligned} \mathbf{e}^{(x)}(\mathbf{q}) &= \sum_{\lambda=1}^2 a^{(\lambda)}(\chi) \mathbf{e}^{(\lambda)}(\mathbf{q}) \\ \mathbf{E}^{(x)}(\mathbf{q}, t) &= \mathcal{E}(t) \mathbf{e}^{(x)}(\mathbf{q}) = \sum_{\lambda=1}^2 a^{(\lambda)}(\chi) \mathbf{E}^{(\lambda)}(\mathbf{q}, t) \\ \mathbf{E}^{(\lambda)}(\mathbf{q}, t) &= \mathcal{E}(t) \mathbf{e}^{(\lambda)}(\mathbf{q}) \end{aligned} \quad (3.9)$$

What is the time-dependence of the field? We can leave it in the completely general form (3.9) for almost all of this calculation, apart from the harmless requirement (see section 5.1) that $\mathcal{E}(t)=0, t < 0$. However, we do have two important special cases in mind:

1. Periodic field of frequency ω : $\mathcal{E}(t) = \mathcal{E}_0 e^{-i\omega t}$
2. Pulsed field “of frequency ω ”: $\mathcal{E}(t) = \mathcal{E}_0(t) e^{-i\omega t}$, in which a periodic variation is multiplied by an envelope function $\mathcal{E}_0(t)$ which we imagine to be peaked at some time t_0 and of duration τ . For example, the envelope function could be a Gaussian: $\mathcal{E}_0(t) \sim e^{-(t-t_0)^2/\tau^2}$. The intension of the quotes above is to remind us that clearly $\mathcal{E}(t)$ now has more than one frequency component.

Thus the interaction becomes

$$\begin{aligned} \mathcal{V}^{(\chi)}(\mathbf{q}, t) &= \sum_{\lambda} a^{(\lambda)}(\chi) \mathcal{V}^{(\lambda)}(\mathbf{q}, t) \\ \mathcal{V}^{(\lambda)}(\mathbf{q}, t) &= \mathcal{E}(t) (\mathbf{e}^{(\lambda)}(\mathbf{q}) \cdot \mathbf{d}) \end{aligned} \quad (3.10)$$

3.2 Basis kets

The most elementary degrees of freedom one can use to describe an electron are momentum and spin, and these are natural observables to use to classify the photoelectron states. The associated state kets are the eigenkets $\{|\mathbf{k}\rangle\}$ of the momentum operator \mathbf{p} and the eigenkets $\{|m_s\rangle\}$ of the s_z operator. The entire electron state space is thus spanned by the tensor product kets $\{|\mathbf{k}, m_s\rangle\}$:

$$|\mathbf{k}, m_s\rangle \equiv |\mathbf{k}\rangle \otimes |m_s\rangle \quad (3.11)$$

such that

$$\begin{aligned} \mathbf{p}|\mathbf{k}, m_s\rangle &= \mathbf{k}|\mathbf{k}, m_s\rangle \\ s_z|\mathbf{k}, m_s\rangle &= m_s|\mathbf{k}, m_s\rangle \end{aligned} \quad (3.12)$$

The orthonormality and completeness rules for these kets are obviously

$$\begin{aligned} \langle \mathbf{k}, m_s | \mathbf{k}', m'_s \rangle &= \delta(\mathbf{k} - \mathbf{k}') \delta_{m_s m'_s} \\ \sum_{m_s} \int d\mathbf{k} |\mathbf{k}, m_s\rangle \langle \mathbf{k}, m_s| &= \mathbf{1} \end{aligned} \quad (3.13)$$

To describe processes involving atomic-like core states, we will also need to use the eigenkets of \mathcal{H}_0 , ie $|n, Q\rangle, |\varepsilon, Q\rangle$, described above, as a basis. In the absence of spin-orbit coupling Q can be taken to include m_s , the eigenvalue of s_z , as in the “uncoupled” representation of (3.3) and (3.4). But in general s_z does not commute with \mathcal{H}_0 and cannot be part of a CSCO involving \mathcal{H}_0 . Indeed, for the spherical atom example outlined above we have energy eigenkets of the following form:

$$\begin{aligned} |n, Q\rangle &= |\varphi_n\rangle \otimes |j, m_j\rangle \\ |\varepsilon, Q\rangle &= |\varphi(\varepsilon)\rangle \otimes |j, m_j\rangle \end{aligned} \quad (3.14)$$

in which $|\varphi_n\rangle$ or $|\varphi(\varepsilon)\rangle$ represents the radial component of the position degree of freedom. Now we know that we can write $|j, m_j\rangle \equiv |l, s, j, m_j\rangle$ in terms of an uncoupled kets $|m_l, m_s\rangle = |l, s, m_l, m_s\rangle$ as follows:

$$|j, m_j\rangle = \sum_{m_l, m_s} |m_l, m_s\rangle \langle m_l, m_s | j, m_j\rangle \quad (3.15)$$

where the quantities $\langle m_l, m_s | j, m_j\rangle \equiv \langle l, s, m_l, m_s | j, m_j\rangle$ are the Clebsch-Gordan coefficients [4].

Thus, we can write the energy eigenkets as a linear combination of uncoupled states:

$$\begin{aligned} |n, Q\rangle &= \sum_{m_l, m_s} |n, m_l, m_s\rangle \langle m_l, m_s | j, m_j\rangle = \sum_{m_l, m_s} |n, m_l\rangle \otimes |m_s\rangle \langle m_l, m_s | j, m_j\rangle \\ |\varepsilon, Q\rangle &= \sum_{m_l, m_s} |\varepsilon, m_l, m_s\rangle \langle m_l, m_s | j, m_j\rangle = \sum_{m_l, m_s} |\varepsilon, m_l\rangle \otimes |m_s\rangle \langle m_l, m_s | j, m_j\rangle \end{aligned} \quad (3.16)$$

Remember, the uncoupled states are **not** themselves eigenkets of \mathcal{H}_0 but only to be used in expanding the energy eigenkets corresponding to eigenvalue ε as in (3.16). But they are eigenkets of \hat{s}_z , unlike the energy eigenkets. And they follow the orthonormality and completeness rules (3.6) and (3.7) with $|n, Q\rangle \rightarrow |n, m_l, m_s\rangle$, $|\varepsilon, Q\rangle \rightarrow |\varepsilon, m_l, m_s\rangle$.

4 The external field - classical polarisation tensor

Suppose that the external electric field takes the form of an ensemble of pure polarisation states χ described by vectors $\mathbf{E}^{(\chi)}(\mathbf{t})$ defined by (3.9) with components along the basis polarisation directions given by

$$E_{\lambda}^{(\chi)}(\mathbf{t}) \equiv \mathbf{E}^{(\chi)}(\mathbf{q}, \mathbf{t}) \cdot \mathbf{e}^{(\lambda)}(\mathbf{q}) = \mathcal{E}(\mathbf{t}) a^{(\lambda)}(\chi) \quad (4.1)$$

and form a matrix \mathbf{J} [5]

$$[\mathbf{J}(\mathbf{t})]_{\lambda\lambda'} \equiv \left\langle \left(E_{\lambda}^{(\chi)}(\mathbf{t}) \right)^* E_{\lambda'}^{(\chi)}(\mathbf{t}) \right\rangle = \sum_{\chi} \rho(\chi) \left(E_{\lambda}^{(\chi)}(\mathbf{t}) \right)^* E_{\lambda'}^{(\chi)}(\mathbf{t}) \quad (4.2)$$

Here $\rho(\chi)$ is the ensemble probability of polarisation χ and so the matrix consists of averages of bilinear products of the field amplitudes. The total average intensity is given by

$$J_{\text{tot}}(\mathbf{t}) \equiv \left\langle \left| E_1^{(\chi)}(\mathbf{t}) \right|^2 + \left| E_2^{(\chi)}(\mathbf{t}) \right|^2 \right\rangle = \text{Tr}[\mathbf{J}(\mathbf{t})] \quad (4.3)$$

We can thus define a matrix $\boldsymbol{\pi}^{(\text{pol})}$

$$\left[\boldsymbol{\pi}^{(\text{pol})}(\mathbf{t}) \right]_{\lambda\lambda'} \equiv \frac{J_{\lambda\lambda'}(\mathbf{t})}{J_{\text{tot}}(\mathbf{t})} = \pi_{\lambda\lambda'}^{(\text{pol})}(\mathbf{t}) \quad (4.4)$$

From (4.2), this matrix is Hermitian and normalised: $Tr[\pi^{(pol)}]=1$ for any time; it is the classical polarisation tensor² of the field [5]. Using (4.1) in (4.2), we can see that

$$J_{\lambda\lambda'}(t) = \mathcal{E}^2(t) \sum_{\chi} p(\chi) a^{(\lambda)*}(\chi) a^{(\lambda')}(\chi)$$

and because $\sum_{\lambda=1}^2 a^{(\lambda)*}(\chi) a^{(\lambda)}(\chi) = 1$ and $\sum_{\chi} p(\chi) = 1$ we also have

$$J_{tot}(t) \equiv \mathcal{E}^2(t)$$

Thus the polarisation tensor for this field is independent of time:

$$[\pi^{(pol)}]_{\lambda\lambda'} = \sum_{\chi} p(\chi) a^{(\lambda)*}(\chi) a^{(\lambda')}(\chi) \quad (4.5)$$

Since $\pi^{(pol)}$ is a 2x2 Hermitian matrix with unit trace, it can be written in terms of the Pauli matrices $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ and a set of 3 real parameters $\xi \equiv (\xi_1, \xi_2, \xi_3)$ in the familiar way [7]:

$$\pi^{(pol)} = \frac{1}{2}(1 + \xi \cdot \sigma) \quad (4.6)$$

Written out explicitly in terms of the 3 real **Stokes parameters** (ξ_1, ξ_2, ξ_3) this becomes

$$\pi^{(pol)} = \frac{1}{2} \begin{pmatrix} 1 + \xi_3 & \xi_1 - i\xi_2 \\ \xi_1 + i\xi_2 & 1 - \xi_3 \end{pmatrix} \quad (4.7)$$

Clearly we can write the tensor for a general, ie mixed, state of polarisation, given by (4.5), as follows:

$$\pi^{[\xi]} = \sum_{\chi} p(\chi) \pi(\chi), \quad [\pi(\chi)]_{\lambda\lambda'} = a^{(\lambda)*}(\chi) a^{(\lambda')}(\chi) \quad (4.8)$$

Here $\pi(\chi)$ is the tensor for a single, pure, state of polarisation, specified by a (complex) unit vector $\mathbf{e}^{(\chi)}(\mathbf{q})$ which is a linear combination of the orthonormal basis vectors $\mathbf{e}^{(1)}, \mathbf{e}^{(2)}$ as in (3.9)

As we can see from Appendix A equation (A.7), the most general (normalised) form for the coefficients is given in terms of two angles α, β :

$$a^{(1)}(\chi) = \cos \alpha, \quad a^{(2)}(\chi) = \sin \alpha e^{i\beta} \quad (4.9)$$

It's easy to work out from (4.8) that the general form for the pure polarisation tensor is

$$\pi(\chi) = \begin{pmatrix} \cos^2 \alpha & \sin \alpha \cos \alpha e^{i\beta} \\ \sin \alpha \cos \alpha e^{-i\beta} & \sin^2 \alpha \end{pmatrix} \quad (4.10)$$

² The counterpart of the polarisation tensor in a treatment in which the field is quantised is, naturally, the photon polarisation density matrix [6]. In fact, expressed in terms of the Stokes parameters, the two quantities are identical.

From this it's clear not only that $\text{tr}[\boldsymbol{\pi}(\chi)] = 1$, but also that $(\boldsymbol{\pi}(\chi))^2 = \boldsymbol{\pi}(\chi)$ and thus $\text{tr}[(\boldsymbol{\pi}(\chi))^2] = 1$. It's clear that the properties of these classical polarisation tensors are identical with those of 2x2 quantum mechanical density matrices for pure and mixed states.

Moreover, comparing (4.7) with (4.10) we see that the Stokes parameters for a pure polarisation state χ are

$$\begin{aligned}\xi_1 &= \sin 2\alpha \cos \beta \\ \xi_2 &= -\sin 2\alpha \sin \beta \\ \xi_3 &= \cos 2\alpha\end{aligned}\tag{4.11}$$

Here are a few special cases:

- $|\boldsymbol{\xi}| = 0$ corresponds to a completely unpolarised state for which $\boldsymbol{\pi}^{(unpol)} = \frac{1}{2} \mathbf{1}$ (any setting of a polarisation detector will transmit half of the light);
- $|\boldsymbol{\xi}| = 1$ corresponds to a pure polarisation state;
- In photoemission lingo, and using our definitions of the basis vectors, s-polarisation corresponds to $\boldsymbol{\xi} = (0, 0, 1)$ and p-polarisation corresponds to $\boldsymbol{\xi} = (0, 0, -1)$. Also, right-hand and left-hand circular polarisation correspond to $\boldsymbol{\xi} = (0, -1, 0)$ and $\boldsymbol{\xi} = (0, 1, 0)$ respectively (see Appendix A). The corresponding polarisation tensors are

$$\begin{aligned}\boldsymbol{\pi}^{(s-pol)} &= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} & \boldsymbol{\pi}^{(p-pol)} &= \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \\ \boldsymbol{\pi}^{(RHC)} &= \frac{1}{2} \begin{pmatrix} 1 & i \\ -i & 1 \end{pmatrix} & \boldsymbol{\pi}^{(LHC)} &= \frac{1}{2} \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix}\end{aligned}\tag{4.12}$$

5 Time evolution

5.1 The initial state

“Initial” means $t = 0$; we'll assume (without loss of generality, I think) that the interaction (ie the external field) is zero for $t < 0$.

We take the state of the electron at $t = 0$ to be $|\Psi(0)\rangle$, an energy eigenstate

$$\mathcal{H}_0 |\Psi(0)\rangle = E_0 |\Psi(0)\rangle$$

Here we assume that $|\Psi(0)\rangle$ is a bound state in the sense that the wave function $\langle \mathbf{r} | \Psi(0) \rangle$ is zero at large distances outside the system. Note that this holds even if the system is large, eg a crystal – in the present context “bound” means spatially confined to the system and “continuum” means able to escape from the system (to infinity). For example, $|\Psi(0)\rangle$ could be an atomic-like core level, or a molecular orbital, or a delocalised band state in a crystal. If we take the initial state to be the n^{th} bound state, then according to (3.16) we can write

$$|\Psi(0)\rangle = \sum_{m_l, m_s} |n, m_l, m_s\rangle \langle m_l, m_s | j, m_j \rangle \quad (5.1)$$

5.2 The state at time t

It's best to use the interaction picture (denoted by [I]) to describe time evolution (see, for example, [1]). In the interaction picture, the time-dependent interaction operator (3.8) becomes

$$\mathcal{V}^{[I]}(t) = e^{i\mathcal{H}_0 t} \mathcal{V}^{[S]}(t) e^{-i\mathcal{H}_0 t} \quad (5.2)$$

Thus, we write (3.8)

$$\mathcal{V}^{(\lambda)}(t) = \mathbf{E}^{(\lambda)}(\mathbf{q}, t) \cdot e^{i\mathcal{H}_0 t} \mathcal{d} e^{-i\mathcal{H}_0 t} = \mathbf{E}^{(\lambda)}(\mathbf{q}, t) \cdot \mathcal{d}(t) \quad (5.3)$$

Here $\mathcal{V}^{(\lambda)}(t)$ and $\mathcal{d}(t)$ are in [I]. From (4.1), we have

$$\mathcal{V}^{(\lambda)}(t) = \sum_{\chi} a^{(\lambda)}(\chi) \mathcal{V}^{(\lambda)}(t); \quad \mathcal{V}^{(\lambda)}(t) = \mathbf{E}^{(\lambda)}(\mathbf{q}, t) \cdot \mathcal{d}(t) \quad (5.4)$$

At time $t > 0$, the system will have evolved into state

$$|\Psi^{(\lambda)}(t)\rangle = U(t, t_0 = 0) |\Psi(0)\rangle \equiv U^{(\lambda)}(t) |\Psi(0)\rangle \quad (5.5)$$

making use of some loose but obvious notational simplifications for the evolution operator:

$U(t, t_0 = 0) \rightarrow U^{(\lambda)}(t)$. We attach the polarisation index χ to the evolution operator and state ket because the former satisfies

$$i \frac{d}{dt} U^{(\lambda)}(t) = \mathcal{V}^{(\lambda)}(\mathbf{q}, t) U^{(\lambda)}(t)$$

Thus

$$\begin{aligned} U^{(\lambda)}(t) &= \mathbf{1} - i \int_0^t dt' \mathcal{V}^{(\lambda)}(\mathbf{q}, t') U^{(\lambda)}(t') \\ &= \mathbf{1} - i \int_0^t dt' \mathcal{V}^{(\lambda)}(\mathbf{q}, t') + (\text{terms of higher order in } \mathcal{V}) \end{aligned} \quad (5.6)$$

In these notes there's no need to go beyond the 1st order approximation in (5.6). Moreover, because $|\Psi(0)\rangle$ cannot contribute to an externally observed photocurrent, by definition, we are not going to be concerned with the component of the evolving ket $|\Psi^{(\lambda)}(t)\rangle$ which remains along $|\Psi(0)\rangle$, only with the rest of $|\Psi^{(\lambda)}(t)\rangle$. So it's convenient, at least for these work-everything-out-in-excruciating-detail notes, to invent some more notation. First, define a "transition" component $|\psi^{(\lambda)}(t)\rangle$ by

$$|\Psi^{(\lambda)}(t)\rangle = |\Psi(0)\rangle + |\psi^{(\lambda)}(t)\rangle \quad (5.7)$$

Note that although the unitarity of the evolution operator guarantees that $|\Psi^{(z)}(t)\rangle$ remains normalised (assuming that $|\Psi(0)\rangle$ is normalised), $|\psi^{(z)}(t)\rangle$ is not normalised. Later we'll calculate $\langle\psi^{(z)}(t)|\psi^{(z)}(t)\rangle$.

Clearly $|\psi^{(z)}(t)\rangle = (1 - \mathcal{P}(0))|\Psi^{(z)}(t)\rangle$, where $\mathcal{P}(0) = |\Psi(0)\rangle\langle\Psi(0)|$ is the projector on to $|\Psi(0)\rangle$. Then if we define the transition component of the evolution operator by

$$U^{(z)}(t) = \mathbf{1} + u^{(z)}(t) \quad (5.8)$$

then clearly

$$|\psi^{(z)}(t)\rangle = u^{(z)}(t)|\Psi(0)\rangle \quad (5.9)$$

Now, using (3.10), (5.4) and (5.6), we can write

$$u^{(z)}(t) = \sum_{\lambda} a^{(\lambda)}(\chi) u^{(\lambda)}(t) \quad (5.10)$$

where

$$u^{(\lambda)}(t) = -i \int_0^t dt' \mathcal{V}^{(\lambda)}(\mathbf{q}, t') \quad (5.11)$$

with $\mathcal{V}^{(\lambda)}$ given by (5.4). Thus, we can write (5.9) as

$$\begin{aligned} |\psi^{(z)}(t)\rangle &= \sum_{\lambda=1}^2 a^{(\lambda)}(\chi) |\psi^{(\lambda)}(t)\rangle \\ |\psi^{(\lambda)}(t)\rangle &= -i \int_0^t dt' \mathcal{E}(t') (e^{(\lambda)}(\mathbf{q}) \cdot \mathcal{d}(t')) |\Psi(0)\rangle \end{aligned} \quad (5.12)$$

Finally, we note the obvious but very important point that the evolution operators described here do not act on the electron spins because the electron-photon interaction does not involve spin.

The ket (5.12) represents the solution of the photoemission problem. $|\psi^{(z)}(t)\rangle$ contains all relevant dependence on the polarisation (and wave vector) of the incident light, and all information about the direction, energy and spin of the photo-emitted electrons. The character of the initial state – usually the main object of interest – is, of course, contained in the initial ket $|\Psi(0)\rangle$, whose calculation is the electronic structure part of the problem.

5.3 The transition amplitudes

This information is extracted from $|\psi^{(z)}(t)\rangle$ by measuring the available observables in the state it represents. This is expressed compactly in the form of **transition amplitudes**

$$\langle \mathbf{k}, m | \psi^{(z)}(t) \rangle = \langle \mathbf{k}, m | u^{(z)}(t) | \Psi(0) \rangle \equiv u_m^{(z)}(\mathbf{k}, t) \quad (5.13)$$

This is clearly the amplitude to find the photoelectron in state $\langle \mathbf{k}, m |$, but we will develop the idea of “finding” the photoelectron properly in the next section. Note that, from (5.12)

$$u_m^{(\lambda)}(\mathbf{k}, t) = \sum_{\lambda=1}^2 a^{(\lambda)}(\chi) u_m^{(\lambda)}(\mathbf{k}, t) \quad (5.14)$$

Note that the norm of $|\psi^{(\lambda)}(t)\rangle$ can be expressed in terms of the transition amplitudes as follows:

$$\langle \psi^{(\lambda)}(t) | \psi^{(\lambda)}(t) \rangle = \sum_m \int dk \langle \psi^{(\lambda)}(t) | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \psi^{(\lambda)}(t) \rangle = \sum_m \int dk |u_m^{(\lambda)}(\mathbf{k}, t)|^2 \quad (5.15)$$

How to calculate the transition amplitudes? Start from (5.13) and (5.11)

$$\begin{aligned} u_m^{(\lambda)}(\mathbf{k}, t) &\equiv \langle \mathbf{k}, m | u^{(\lambda)}(t) | \Psi(0) \rangle = \sum_{\lambda} a^{(\lambda)}(\chi) \langle \mathbf{k}, m | u^{(\lambda)}(t) | \Psi(0) \rangle \\ &= -i \int_0^t dt' \sum_{\lambda} a^{(\lambda)}(\chi) \langle \mathbf{k}, m | \mathcal{V}^{(\lambda)}(\mathbf{q}, t') | \Psi(0) \rangle \end{aligned} \quad (5.16)$$

Here we see the electron-photon matrix elements we expect to find in the theory. In Appendix B we found an expression (B.7) for the interaction $\mathcal{V}^{(\lambda)}$ in real space, expanded in spherical harmonics. This is clearly useful when the initial state $|\Psi(0)\rangle$ is atomic-like, perhaps a core state. But many other forms of initial state can be expanded in spherical harmonics, as can the free photoelectron states $|\mathbf{k}, m\rangle$ - see for example [1]. In any event, the nature of the calculation of the electron states depends on the system under consideration; that's the electronic structure part of the problem. We won't pursue this here, where our focus is the general description of the photoemission process itself³. For now, note that all the traditional selection rules for light-excited electronic transitions are clearly included in (5.16), and that spin does not appear in the interaction $\mathcal{V}^{(\lambda)}$.

6 The process of photoelectron detection

What is actually done when a spin-resolved photoemission spectrum is measured? An idealised time-resolved experiment would have three stages:

1. the photoelectrons hit a screen with a small aperture, which transmits a beam of electrons with a relatively well-defined solid angle of emission $(\theta_k, \phi_k) \equiv \mathbf{k}$, where \mathbf{k} is a unit vector in the direction of emission;
2. this beam enters an energy analyser which in turn filters out all electrons except those with relatively well-defined energy ε - by definition this energy lies in the continuous part of the electron energy eigenvalue spectrum (3.5), so that $\varepsilon \geq 0$;
3. the spin component, along some direction given by a unit vector \mathbf{n} , of these filtered electrons is measured.

These measurements all involve observables that commute with each other. We assume that all these three processes occur at time t , or, more precisely, that the time lag between the stages of measurement is small enough to be neglected. Note that stage 1 measures the polar angles of the

³ I hope to post another set of notes linking in more detail this general formulation with the electronic structure aspects of photoemission calculations.

electron momentum and stage 2 measures its magnitude, via $\varepsilon = \frac{1}{2}|\mathbf{k}|^2$; thus all three components of momentum have been measured in a detector placed at some position \mathbf{R} outside the crystal. This sounds like it violates the uncertainty principle – after all, the aperture in stage 1 can be made arbitrarily small, in principle. However, stage 1 only measures two components of the momentum; the third component is measured in stage 2, the energy analyser, which is essentially macroscopic in position space and presumably can't be made arbitrarily small. So all is well.

As a matter of fact, it's quite interesting to analyse the detection process from the space-time point of view à la Feynman [8]. But for our present purposes, it seems enough to regard stages 1 and 2 as amounting to a measurement of the full momentum $\mathbf{k} \equiv (\hat{\mathbf{k}}, |\mathbf{k}|^2 = 2\varepsilon)$ of the photoelectron.

6.1 Measuring momentum

Thus we can represent these stages by suitably defined operators in the following way. First, we use the momentum-spin basis $\{|\mathbf{k}, m\rangle\}$ defined in section 3.2 for the photoelectron ket space. Here, remember, \mathbf{k} is the momentum of the photoelectron and m is the eigenvalue of s_z (the spin operator along the crystal z-axis). Stages 1 and 2 are then represented by the following projector [9]

$$\begin{aligned} \mathcal{P}(\mathbf{k}) &= \int_{\theta_k - \Delta_\theta}^{\theta_k + \Delta_\theta} \sin\theta_{k'} d\theta_{k'} \int_{\phi_k - \Delta_\phi}^{\phi_k + \Delta_\phi} d\phi_{k'} \int_{k - \Delta_k}^{k + \Delta_k} dk' k'^2 \sum_m |\mathbf{k}', m\rangle \langle \mathbf{k}', m| \\ &= \int_{k - \Delta_k}^{k + \Delta_k} dk' \sum_m |\mathbf{k}', m\rangle \langle \mathbf{k}', m| = \int_{k - \Delta_k}^{k + \Delta_k} dk' |\mathbf{k}'\rangle \langle \mathbf{k}'| \otimes \mathcal{I}_3 \end{aligned} \quad (6.1)$$

The quantities $\Delta_\theta, \Delta_\phi, \Delta_k$ represent the finite angle and radial resolution of the momentum measurement and their product defines what one might call the “resolution volume” Ω in momentum space (see Appendix C). In (6.1) we also introduced an obvious shorthand notation for the full integral. \mathcal{I}_3 is the unit operator in spin space; $\mathcal{P}(\mathbf{k})$ is the extension of a k-space operator into the full momentum-spin product space [2].

Now before the measurement, the system is described by the time-evolved ket $|\psi^{(x)}(t)\rangle$ in (5.9).

Following the measurement, according to the 5th postulate of quantum mechanics [2], the state of the system is described by the following normalised projection:

$$|\psi^{(x)}(\mathbf{k}, t)\rangle = \frac{\mathcal{P}(\mathbf{k})|\psi^{(x)}(t)\rangle}{\sqrt{\langle \psi^{(x)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(x)}(t) \rangle}} \quad (6.2)$$

Some care has to be exercised in using this projector. In Appendix C we discuss the general issue of projectors in a continuous state space, and in particular, derive the following results for matrix elements between arbitrary kets:

$$\langle \psi | \mathcal{P}(\mathbf{k}) | \psi' \rangle = \Omega \sum_m \langle \psi | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \psi' \rangle = \langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{P}(\mathbf{k}) | \psi' \rangle \quad (6.3)$$

Here the resolution volume Ω appears. Note that (6.3) ensures that the projected ket $|\psi^{(x)}(\mathbf{k}, t)\rangle$ in (6.2) is indeed normalised.

Note that the total probability $P_{\text{tot}}(\chi; \mathbf{k}, t)$ of exciting a photoelectron of momentum \mathbf{k} and any spin with light of polarisation χ is just

$$P_{\text{tot}}(\chi; \mathbf{k}, t) = \langle \psi^{(\chi)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(\chi)}(t) \rangle = \Omega \sum_m \langle \psi^{(\chi)}(t) | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \psi^{(\chi)}(t) \rangle \quad (6.4)$$

This probability is, of course, proportional to the resolution volume. Let's define the corresponding probability density, or, as we shall call it, **spectral weight**, $W(\chi; \mathbf{k}, t)$ by

$$P_{\text{tot}}(\chi; \mathbf{k}, t) \equiv \Omega W(\chi; \mathbf{k}, t) \quad (6.5)$$

From (6.4) and using (5.13) and (5.14), we have

$$\begin{aligned} W(\chi; \mathbf{k}, t) &= \sum_m \langle \psi^{(\chi)}(t) | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \psi^{(\chi)}(t) \rangle \\ &= \sum_m |u_m^{(\chi)}(\mathbf{k}, t)|^2 = \sum_m \sum_{\lambda\lambda'} a^{(\lambda)*}(\chi) a^{(\lambda')}(\chi) u_m^{(\lambda)*}(\mathbf{k}, t) u_m^{(\lambda')}(\mathbf{k}, t) \end{aligned} \quad (6.6)$$

Now introducing the polarisation tensor $\pi(\chi)$ defined in (4.8), we obtain

$$W(\chi; \mathbf{k}, t) = \sum_m \sum_{\lambda\lambda'} [\pi(\chi)]_{\lambda'\lambda} u_m^{(\lambda)*}(\mathbf{k}, t) u_m^{(\lambda')}(\mathbf{k}, t)$$

This is the first appearance of what we might call the **transition probability matrix** $\mathbf{T}(\mathbf{k}, t)$

$$[\mathbf{T}(\mathbf{k}, t)]_{mm'}^{\lambda\lambda'} = u_m^{(\lambda)*}(\mathbf{k}, t) u_{m'}^{(\lambda')}(\mathbf{k}, t) \quad (6.7)$$

Thus

$$W(\chi; \mathbf{k}, t) = \sum_m \sum_{\lambda\lambda'} [\pi(\chi)]_{\lambda'\lambda} [\mathbf{T}(\mathbf{k}, t)]_{mm}^{\lambda\lambda'} \quad (6.8)$$

Here we have a nice separation between the possible transitions that light of any polarisation can excite, represented by $\mathbf{T}(\mathbf{k}, t)$, and the actual polarisation state of the light, represented by $\pi(\chi)$. The transition probability matrix contains all the information about all possible observations of the photoelectron, as we shall see. It is a 4-dimensional matrix; therefore tracing over either the polarisation or spin indices produces a 2x2 matrix:

$$\begin{aligned} \text{Trace over polarisations: } & [\text{Tr}^{[\lambda]} \{\mathbf{T}\}]_{mm'} \equiv \sum_{\lambda=1}^2 [\mathbf{T}]_{mm'}^{\lambda\lambda} \\ \text{Trace over spins: } & [\text{Tr}^{[m]} \{\mathbf{T}\}]^{\lambda\lambda'} \equiv \sum_{m=-1/2}^{1/2} [\mathbf{T}]_{mm}^{\lambda\lambda'} \end{aligned} \quad (6.9)$$

Thus, we can write (6.8) as follows:

$$W(\chi; \mathbf{k}, t) = \sum_m [\text{Tr}^{[\lambda]} \{\pi(\chi) \mathbf{T}(\mathbf{k}, t)\}]_{mm} = \text{Tr}^{[m]} \{ \text{Tr}^{[\lambda]} \{\pi(\chi) \mathbf{T}(\mathbf{k}, t)\} \} \quad (6.10)$$

6.2 Measuring spin

Suppose we have detected a photoelectron with momentum \mathbf{k} by the kind of process described in section 6.1. We can perform further measurements on this photoelectron - for example determining its spin. The result of a measurement corresponding to an observable \mathcal{A} will be given by taking the expectation value of \mathcal{A} in the ket $|\psi^{(z)}(\mathbf{k}, t)\rangle$ in (6.2):

$$\langle \mathcal{A} \rangle(\mathbf{k}, t) = \langle \psi^{(z)}(\mathbf{k}, t) | \mathcal{A} | \psi^{(z)}(\mathbf{k}, t) \rangle = \frac{\langle \psi^{(z)}(t) | \mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k}) | \psi^{(z)}(t) \rangle}{\langle \psi^{(z)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(z)}(t) \rangle} \quad (6.11)$$

Appendix C shows how to calculate matrix elements of the kind needed in (6.11)⁴. Here we'll see how this works when the observable \mathcal{A} is a spin component.

Photoelectron spin is measured by some kind of polarimeter (a Mott detector, or suchlike), which can be thought of as a filter⁵ which passes electrons with spins oriented in a certain direction specified by unit vector $\hat{\mathbf{n}}$. The spin-resolved spectrum is then found from the expectation value of $s \cdot \mathbf{n}$ in the ket $|\psi^{(z)}(\hat{\mathbf{k}}, \varepsilon, t)\rangle \equiv |\psi^{(z)}(\mathbf{k}, t)\rangle$ given in (6.2), where

$$s \cdot \mathbf{n} = \sum_{\mu=1}^3 s_{\mu} n_{\mu}, \quad \mu = \text{Cartesian coordinate index} \quad (6.12)$$

Then, according to (6.11) the expectation value

$$\langle s_{\mu} \rangle(\chi; \mathbf{k}, t) = \frac{\langle \psi^{(z)}(t) | \mathcal{P}(\mathbf{k}) s_{\mu} \mathcal{P}(\mathbf{k}) | \psi^{(z)}(t) \rangle}{\langle \psi^{(z)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(z)}(t) \rangle} \quad (6.13)$$

measures the μ -component of the spin in a photoelectron state with momentum \mathbf{k} (at time t). Using the results of Appendix C (6.1) and (5.13), we get the normalising denominator in (6.13) in terms of the transition amplitudes:

$$\begin{aligned} \langle \psi^{(z)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(z)}(t) \rangle &= \int_{\mathbf{k}-\Delta\mathbf{k}}^{\mathbf{k}+\Delta\mathbf{k}} d\mathbf{k}' \sum_m \langle \psi^{(z)}(t) | \mathbf{k}', m \rangle \langle \mathbf{k}', m | \psi^{(z)}(t) \rangle \\ &= \Omega \sum_m \left| \langle \mathbf{k}, m | \psi^{(z)}(t) \rangle \right|^2 = \Omega \sum_m |u_m^{(z)}(\mathbf{k}, t)|^2 \end{aligned} \quad (6.14)$$

Similarly, we can write the numerator of (6.13) as follows:

$$\langle \psi^{(z)}(t) | \mathcal{P}(\mathbf{k}) s_{\mu} \mathcal{P}(\mathbf{k}) | \psi^{(z)}(t) \rangle = \Omega \sum_{m, m'} u_m^{(z)*}(\mathbf{k}, t) u_{m'}^{(z)}(\mathbf{k}, t) \left[\frac{1}{2} \sigma_{\mu} \right]_{m, m'} \quad (6.15)$$

Here σ_{μ} is the μ -component Pauli matrix. Thus the expectation value of the spin in (6.13) is simply

⁴ This is an example of defining an operator, $\mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k})$, whose action is restricted to a subspace of the entire state space. The formal mathematics of this is explained by Cohen-Tannoudji et al [2] with their usual care. My argument here is meant to give a more physical flavour to the procedure.

⁵ In fact, this represents an ideal measurement in which the filtering occurs with perfect efficiency. There is a quite neat formalism (see [10]) for describing less ideal measurements – the so-called efficiency matrix. However, it doesn't really add much to the discussion here, so the reference will have to suffice.

$$\langle s_\mu \rangle(\chi; \mathbf{k}, t) = \frac{\sum_{m, m'} \left[\frac{1}{2} \sigma_\mu \right]_{m, m'} u_{m'}^{(\chi)}(\mathbf{k}, t) u_m^{(\chi)*}(\mathbf{k}, t)}{\sum_m |u_m^{(\chi)}(\mathbf{k}, t)|^2} \quad (6.16)$$

But this is the trace over spin of a matrix product

$$\langle s_\mu \rangle(\chi; \mathbf{k}, t) = \text{Tr}^{[m]} \left\{ \frac{1}{2} \sigma_\mu \rho^{(s)}(\chi; \mathbf{k}, t) \right\} \quad (6.17)$$

We identify the *spin density matrix* of the photoelectron as

$$\left[\rho^{(s)}(\chi; \mathbf{k}, t) \right]_{m', m} = \frac{u_{m'}^{(\chi)}(\mathbf{k}, t) u_m^{(\chi)*}(\mathbf{k}, t)}{\sum_m |u_m^{(\chi)}(\mathbf{k}, t)|^2} \quad (6.18)$$

Clearly $\text{Tr}^{[m]} \{ \rho^{(s)}(\chi; \mathbf{k}, t) \} = 1$. Now we could have calculated the spin density matrix directly as a reduction of the full density operator $\rho(\chi; \mathbf{k}, t) = |\psi^{(\chi)}(\mathbf{k}, t)\rangle \langle \psi^{(\chi)}(\mathbf{k}, t)|$ by tracing out the momentum dependence. Let's show that this procedure gives the same result as (6.18). From (6.2) we have

$$\rho(\chi; \mathbf{k}, t) = \frac{\mathcal{P}(\mathbf{k}) |\psi^{(\chi)}(t)\rangle \langle \psi^{(\chi)}(t)| \mathcal{P}(\mathbf{k})}{\langle \psi^{(\chi)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(\chi)}(t) \rangle}$$

Hence

$$\left[\rho^{(s)}(\chi; \mathbf{k}, t) \right]_{m_1, m_2} = \left[\text{Tr}^{[k]} \rho(\chi; \mathbf{k}, t) \right]_{m_1, m_2} \equiv \int_{-\infty}^{\infty} d\mathbf{k}' \frac{\langle \mathbf{k}', m_1 | \mathcal{P}(\mathbf{k}) | \psi^{(\chi)}(t) \rangle \langle \psi^{(\chi)}(t) | \mathcal{P}(\mathbf{k}) | \mathbf{k}', m_2 \rangle}{\langle \psi^{(\chi)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(\chi)}(t) \rangle}$$

In Appendix C we show that

$$\int_{-\infty}^{\infty} d\mathbf{k}' \langle \mathbf{k}', m_1 | \mathcal{P}(\mathbf{k}) | \psi^{(\chi)}(t) \rangle \langle \psi^{(\chi)}(t) | \mathcal{P}(\mathbf{k}) | \mathbf{k}', m_2 \rangle = \Omega \langle \mathbf{k}', m_1 | \psi^{(\chi)}(t) \rangle \langle \psi^{(\chi)}(t) | \mathbf{k}', m_2 \rangle$$

and that

$$\langle \psi^{(\chi)}(t) | \mathcal{P}(\mathbf{k}) | \psi^{(\chi)}(t) \rangle = \Omega \sum_m \left| \langle \mathbf{k}, m | \psi^{(\chi)}(t) \rangle \right|^2$$

Thus, writing this in terms of the transition amplitudes (5.13), we obtain exactly our previous result (6.18).

7 How spectra depend on polarisation

The formalism developed above is very general; it allows the full spin and angle resolved photoemission spectrum to be calculated for any polarisation state and time-dependence of the exciting light field. An important part of the physics of this, to reiterate, is that although the electron spin does not appear in the electron-light interaction, the polarisation of the light couples to the

orbital angular momentum of the electron, and thus spin-orbit coupling may link light polarisation to photoelectron spin indirectly.

In this section, we consider experiments in which the spin is not measured. Photoemission spectra usually do depend on the polarisation of the light used, simply because of the usual orbital angular momentum selection rules – see Appendix B . In magnetic systems, a different type of polarisation-dependence may arise due to the lifting of degeneracies in the presence of a magnetic moment. In this way, photoemission spectra may exhibit a kind of magnetic dichroism [11].

If the spin is not measured, the total probability density for exciting a photoelectron of momentum \mathbf{k} and any spin with light of polarisation χ is (see (6.10))

$$W(\chi; \mathbf{k}, t) = \sum_m \left[\text{Tr}^{[\lambda]} \{ \Pi(\chi) \mathbf{T}(\mathbf{k}, t) \} \right]_{mm} = \text{Tr}^{[m]} \left\{ \text{Tr}^{[\lambda]} \{ \Pi(\chi) \mathbf{T}(\mathbf{k}, t) \} \right\} \quad (7.1)$$

Thus

$$W(\chi; \mathbf{k}, t) = \text{Tr}^{[\lambda]} \left[\Pi(\chi) \boldsymbol{\tau}(\mathbf{k}, t) \right] \quad (7.2)$$

where $\boldsymbol{\tau}(\mathbf{k}, t)$ is a 2x2 matrix in the polarisation indices which we can choose to refer to the s- and p-polarisation basis vectors defined in Appendix A

$$\boldsymbol{\tau}(\mathbf{k}, t) = \begin{pmatrix} \tau^{ss} & \tau^{sp} \\ \tau^{ps} & \tau^{pp} \end{pmatrix}, \quad \tau^{\lambda'\lambda} = \sum_m \left[\mathbf{T}(\mathbf{k}, t) \right]_{mm}^{\lambda'\lambda} = \text{Tr}^{[m]} \{ \mathbf{T}(\mathbf{k}, t) \} \quad (7.3)$$

Using the rules for the Stokes parameters given in section 4, we can now collect in Table 1 below the rules showing how to calculate the spectra corresponding to common polarisation states.

Now photoemission spectra, spin-resolved or not, generally depend on the polarisation of the light, show dichroism in other words, due to the usual selection rules and geometrical factors; all this is built in to the above formulae, of course. However, spin-orbit coupling may lead to additional dependence on polarisation. In magnetic systems, spectra may show dichroism where the corresponding non-magnetic systems would not, a kind of magnetic dichroism in fact, and this may be a useful way to probe magnetic systems without actually spin-resolving the spectra. It's actually a very rich picture, and is best illustrated by actual calculations, eg [11].

Polarisation	$W(\chi; \mathbf{k}, t)$
Unpolarised	$\frac{1}{2} (\tau^{ss} + \tau^{pp})$
s-polarised	τ^{ss}
p-polarised	τ^{pp}
Right-hand circularly polarised	$\frac{1}{2} \left[(\tau^{ss} + \tau^{pp}) - i (\tau^{sp} - \tau^{ps}) \right]$
Left-hand circularly polarised	$\frac{1}{2} \left[(\tau^{ss} + \tau^{pp}) + i (\tau^{sp} - \tau^{ps}) \right]$

Table 1

Note that, from (6.7), $\boldsymbol{\tau}(\mathbf{k}, t)$ is Hermitian, ie $\tau^{\lambda'\lambda} = (\tau^{\lambda\lambda'})^*$, so that W in Table 1 is always real.

8 How spectra depend on spin

Without further algebra, one can see from (5.9) that spin-orbit coupling enters this problem only through the initial state $|\Psi(0)\rangle$ and the Hamiltonian \mathcal{H}_0 which controls the time evolution of the electron system; the evolution operator itself only contains the electron-photon interaction which is independent of spin. Now suppose spin-orbit coupling is neglected in $|\Psi(0)\rangle$ - for example, the initial state might be a $s_{1/2}$ core level and spin-orbit coupling might be negligible at photoelectron energies. Then $|\psi^{(\lambda)}(t)\rangle$ is an eigenket of s_z with the same eigenvalue m_0 as the initial state (ie $|\psi(0)\rangle = |n, m_i\rangle \otimes |m_0\rangle$), and the tensor defined in (6.7) has the form

$$T_{mm'}^{\lambda\lambda'}(\mathbf{k}, t) = T_{m_0 m_0}^{\lambda\lambda'}(\mathbf{k}, t) \delta_{m, m_0} \delta_{m', m_0} \quad (8.1)$$

In this case, spin-polarisation of the spectrum could only arise if the spin-up and spin-down states were non-degenerate, as in a magnetic system. Otherwise, the spin-up and spin-down spectra would be identical and no net spin-polarisation could be seen in the spectra.

It is easy to see, then, that if spin-orbit coupling were neglected in the way described above, the spin density matrix has the form – see (8.1):

$$\left[\rho^{[S]}(\chi; \mathbf{k}, t) \right]_{mm'} = \delta_{m, m_0} \delta_{m', m_0} \quad (8.2)$$

Therefore (6.17) implies that without spin-orbit coupling $\langle s_x \rangle(\chi; \mathbf{k}, t) = 0 = \langle s_y \rangle(\chi; \mathbf{k}, t)$, whatever the spin m_0 of the initial state $|\psi(0)\rangle$, while $\langle s_z \rangle(\chi; \mathbf{k}, t) = m_0$. This is all very natural.

Thus, regarding the spin-polarisation of the spectrum, the position can be summarised as follows:

1. For non-magnetic systems, there is no spin-polarisation in the absence of spin-orbit coupling.
2. For non-magnetic systems, spin-orbit coupling in either the initial state or the final state or both will generally give rise to spin-polarised spectra, depending on the polarisation of the light (see [11]).
3. For systems with permanent magnetic moments, the spin-up and spin-down electron states are non-degenerate and this can give rise to spin-polarised spectra even without spin-orbit coupling.

Since (6.18) defines a normalised 2x2 Hermitian matrix, the spin density matrix can be written in the form [7]

$$\rho^{(S)}(\chi; \mathbf{k}, t) = \frac{1}{2}(\mathbf{1} + \mathbf{M}(\chi; \mathbf{k}, t) \cdot \boldsymbol{\sigma}) \quad (8.3)$$

where the **spin polarisation** vector \mathbf{M} is given by

$$M_\mu(\chi; \mathbf{k}, t) = \text{Tr}^{[m]} \left\{ \rho^{(S)}(t) \boldsymbol{\sigma}_\mu \right\} = 2 \langle s_\mu \rangle(\chi; \mathbf{k}, t), \quad \mu = x, y, z \quad (8.4)$$

This follows immediately from the properties of the Pauli matrices [7]. Thus if we measure the photoelectron spin component along a direction given by unit vector $\mathbf{n} = (n_x, n_y, n_z)$ we have

$$\langle s \cdot \mathbf{n} \rangle(\chi; \mathbf{k}, t) = \sum_\mu n_\mu \langle s_\mu \rangle(\chi; \mathbf{k}, t) \quad (8.5)$$

From (8.4), then, we have

$$\langle s \cdot \mathbf{n} \rangle(\chi; \mathbf{k}, t) = \frac{1}{2} \mathbf{n} \cdot \mathbf{M}(\chi; \mathbf{k}, t) \quad (8.6)$$

This nice result tells us how to determine the spin-polarisation \mathbf{M} by changing the orientation of the spin detector.

Thus, we now have both a way of calculating the photoelectron spin density matrix (section 6.2) and a protocol for determining it experimentally – measure the spin polarisation \mathbf{M} .

9 How spectra depend on time

9.1 The transition amplitudes

Now we calculate the time-dependence of the evolution amplitudes $u_m^{(\lambda)}(\mathbf{k}, t)$ given by equation (5.13). Inserting a complete set of electron energy eigenkets (3.7), a move pretty well forced by the presence of $e^{-i\mathcal{H}_0 t}$, we find from (3.7), (5.3) and (5.11)

$$\begin{aligned} u_m^{(\lambda)}(\mathbf{k}, t) &= -i \int_0^t dt' \langle \mathbf{k}, m | \mathcal{E}(t') (\mathbf{e}^{(\lambda)}(\mathbf{q}) \cdot \mathcal{d}(t')) | \Psi(0) \rangle \\ &= -i \sum_Q \int_0^\infty d\varepsilon \int_0^t dt' \mathcal{E}(t') \langle \mathbf{k}, m | \varepsilon, Q \rangle \langle \varepsilon, Q | (\mathbf{e}^{(\lambda)}(\mathbf{q}) \cdot e^{i\mathcal{H}_0 t'} \mathcal{d} e^{-i\mathcal{H}_0 t'}) | \Psi(0) \rangle \\ &= -i \sum_Q \int_0^\infty d\varepsilon \int_0^t dt' \mathcal{E}(t') e^{i(\varepsilon - E_0)t'} \langle \mathbf{k}, m | \varepsilon, Q \rangle \langle \varepsilon, Q | (\mathbf{e}^{(\lambda)}(\mathbf{q}) \cdot \mathcal{d}) | \Psi(0) \rangle \end{aligned}$$

Recall that E_0 is the energy eigenvalue of the initial state. But we must have

$$\langle \mathbf{k}, m | \varepsilon, Q \rangle = C_{m,Q}(\mathbf{k}) \delta(\varepsilon - E), \quad E = \frac{k^2}{2} \quad (9.1)$$

I have the following argument for this statement. The quantities $\langle \mathbf{k}, m | \varepsilon, Q \rangle$ are the coefficients in an expansion of the energy eigenket⁶ in momentum eigenkets (3.12). Therefore they are also the coefficients in an expansion of the corresponding position space wave functions:

$$\langle \mathbf{r} | \varepsilon, Q \rangle = \int d\mathbf{k} \sum_m \langle \mathbf{r} | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \varepsilon, Q \rangle$$

But we know that for positions \mathbf{R} outside the range of the binding potential in the electron system (such as the location of the instruments detecting and measuring the photoelectron) the energy eigenfunction is a linear combination of free space momentum eigenfunctions with $|\mathbf{k}|^2 = k^2 = 2\varepsilon$. Therefore (9.1) must hold.

As a result of (9.1), then, we have

$$u_m^{(\lambda)}(\mathbf{k}, t) = -i \sum_Q \int_0^t dt' \mathcal{E}(t') e^{i(E - E_0)t'} C_{m,Q}(\mathbf{k}) \langle \varepsilon, Q | (\mathbf{e}^{(\lambda)}(\mathbf{q}) \cdot \mathcal{d}) | \Psi(0) \rangle \quad (9.2)$$

To tidy this up a bit, define

⁶ As noted in section 3.1, the states $|\varepsilon, Q\rangle$ are scattering states, solutions of the Lipmann-Schwinger equation. When dealing with the surface of a crystal, Pendry called them “time-reversed LEED states”.

$$d_m^{(\lambda)}(\mathbf{k}) \equiv \sum_Q C_{m,Q}(\mathbf{k}) \langle E, Q | \mathbf{e}^{(\lambda)}(\mathbf{q}) \cdot \mathcal{A} | \Psi(0) \rangle \quad (9.3)$$

and

$$f(E, t) \equiv -i \int_0^t dt' \mathcal{E}(t') e^{i(E-E_0)t'} \quad (9.4)$$

Thus

$$u_m^{(\lambda)}(\mathbf{k}, t) = d_m^{(\lambda)}(\mathbf{k}) f(E, t) \quad (9.5)$$

9.2 Time-dependent spectra

Using this expression in (6.7) we find

$$\begin{aligned} T_{mm'}^{\lambda\lambda'}(\mathbf{k}, t) &= D_{mm'}^{\lambda\lambda'}(\mathbf{k}) |f(E, t)|^2 \\ D_{mm'}^{\lambda\lambda'}(\mathbf{k}) &\equiv d_m^{(\lambda)}(\mathbf{k}) d_{m'}^{(\lambda')*}(\mathbf{k}) \end{aligned} \quad (9.6)$$

Equations (9.4) and (9.6) account for a general time-dependent field. We now consider in more detail the two important special cases mentioned in section 3.1.

Periodic field

If $\mathcal{E}(t) = \mathcal{E}_0 e^{-i\omega t}$, we recover the standard Golden Rule form for the transition rate induced by a periodic perturbation. It's easy to see that

$$\begin{aligned} f(E, t) &= \mathcal{E}_0 e^{i(E-E_0-\omega)t} \frac{\sin(E-E_0-\omega)t}{E-E_0-\omega} \\ |f(E, t)|^2 &= \mathcal{E}_0^2 \frac{\sin^2(E-E_0-\omega)t}{(E-E_0-\omega)^2} \end{aligned} \quad (9.7)$$

The usual somewhat shabby trick is to observe that $\lim_{t \rightarrow \infty} |f(E, t)|^2 = 2\pi t \delta(E-E_0-\omega)$. This can be made less shabby (see, for example, [13]) by observing from (9.7) that $|f(E, t)|^2$ is strongly peaked at $E = E_0 + \omega$ with a width of order t^{-1} . Then, if the energy resolution is not too good, ie $\Delta E \gg t^{-1}$ we can approximate

$$\int_{E_1+\omega-\Delta E}^{E_1+\omega+\Delta E} dE' \frac{\sin^2(E'-E_1-\omega)t}{(E'-E_1-\omega)^2} \approx \int_{-\infty}^{\infty} dx \frac{\sin^2(xt)}{x^2} = \pi t \quad (9.8)$$

So, as usual, from this we obtain the same result as if we'd used the shabby delta function expression, but we don't have to feel bad about it.

Pulsed field

Suppose the function $\mathcal{E}(t)$ represents a pulse of the kind described in section 3.1, ie a periodic variation modulated by a peaked envelope function $\mathcal{E}(t) = \mathcal{E}_0(t)e^{-i\omega t}$. If the peak of the pulse occurs well after $t=0$ then for long times, we encounter the Fourier transform of $\mathcal{E}_0(t)$:

$$\lim_{t \rightarrow \infty} f(E, t) = -i\tilde{\mathcal{E}}_0(E - \omega - E_0) \quad (9.9)$$

$$\tilde{\mathcal{E}}_0(\nu) = \int_{-\infty}^{\infty} dt e^{i\nu t} \mathcal{E}_0(t)$$

As we know from studying the excitation and dynamics of wave packets (see [14], [15]), the physics of this is as follows. Suppose the field pulse has duration τ . If we follow the evolution of the state ket using (5.5) and (5.6), we find that the ket acquires an excited component which evolves in time into an outgoing wave packet – the photoelectron – consisting of a superposition of energy eigenstates with energies peaked around $\omega + E_1$ and with an energy spread of $\sim \tau^{-1}$. This is why the Fourier transform (9.9) shows up in the transition rate.

10 Summing over the initial states

Sometimes we know the initial state from which photoexcitation has occurred, often (eg in core level photoemission) because the eigenvalue spectrum makes it fairly obvious. In principal, however, we don't know this information, and we must sum over all possible initial states.

The first step in this is to give the tensor (6.7) or (9.6) an index labelling the initial state to which it corresponds:

$$\mathbf{T} \rightarrow \mathbf{T}_I \quad (10.1)$$

Given the nature of the initial state, see (5.1), we can see that the corresponding tensor must, in general, be a function of the energy E_I and the remaining quantum numbers – eg (m_l, m_s) or (j, m_j) in (5.1). Give these remaining quantum numbers the collective index \mathbf{Q}_i . Thus the energy eigenvalue is, in general, to be labelled by \mathbf{Q}_i and an index n which might specify the principal quantum number in a core level or something analogous like a band index. We can write

$$\mathbf{T}_I = \mathbf{T}_{\mathbf{Q}_i}(E_I) = \mathbf{T}_{\mathbf{Q}_i}(E_{n, \mathbf{Q}_i}) \quad (10.2)$$

Now we can write the full tensor summed over initial states in terms of a projected or partial density of states:

$$\mathbf{T} \equiv \sum_I \mathbf{T}_I = \sum_{n, \mathbf{Q}_i} \mathbf{T}_{\mathbf{Q}_i}(E_{n, \mathbf{Q}_i}) = \sum_{\mathbf{Q}_i} \int d\varepsilon \sum_n \delta(\varepsilon - E_{n, \mathbf{Q}_i}) \mathbf{T}_{\mathbf{Q}_i}(\varepsilon)$$

Or

$$\mathbf{T} = \sum_{\mathbf{Q}_i} \int d\varepsilon n_{\mathbf{Q}_i}(\varepsilon) \mathbf{T}_{\mathbf{Q}_i}(\varepsilon) \quad (10.3)$$

where

$$n_{\mathbf{q}_i}(\varepsilon) = \sum_n \delta(\varepsilon - E_{n,\mathbf{q}_i}) \quad (10.4)$$

Now, if for a periodic field, we insert the Golden rule result into (9.6), we easily obtain

$$\mathbf{T} \simeq 2\pi t \Delta_k \sum_{\mathbf{q}_i} n_{\mathbf{q}_i}(E - \omega) \mathbf{D}_{\mathbf{q}_i}(E - \omega) \quad (10.5)$$

in which \mathbf{D} is the tensor symbol for $D_{m_s, m'_s}^{\lambda\lambda'}$ in (9.6). Thus the full spectrum is a sum of contributions from each set of quantum numbers \mathbf{Q}_i weighted by the corresponding partial density of states. Some of these contributions will probably be zero by virtue of the selection rules embedded in the matrix elements (9.3) and thus in the tensor \mathbf{D} .

11 Post-amble

Perhaps it's worth briefly summarising the aims of this note and what its main results are. We started with the idea of providing, at the 1-electron level, a fairly comprehensive and general theoretical description of the photoemission process itself. This was motivated by experimental developments associated with exploiting the polarisation and pulsed nature of modern light sources, together with the capability of measuring the spin of photoelectrons. These aspects were naturally not in focus when the original first-principles calculations of angle-resolved photoemission were made in the 1970s and 1980s, so it seemed worthwhile to fill them in now. We did this by formulating the photon part of the problem in terms of the polarisation tensor, and the electron spin part in terms of the photoelectron spin density matrix. We worked out general formulae by which the angle-resolved photoemission spectral weight and spin density matrix can be found, as a function of time, from the usual experimental parameters – photon energy, incidence angles and Stokes parameters. Obviously, there are many input parameters for the experimentalist to adjust here, as well as a wealth of measurable properties of the emitted electrons – it's a richly detailed picture, certainly, but this is what gives photoemission its special power. We cast our general formulae in terms of a set of transition amplitudes linking the initial states to plane-wave photoelectron states, and we combined these amplitudes, dyadic-wise, into a transition probability matrix or tensor, which contains all information about all the electron-photon transitions that can be excited in the system. The experimental conditions in any given measurement then determine which of these transitions actually contribute to the observed spectral weight. See Vasilyev et al [16] for a recent take on such questions.

What we did not seriously consider here, apart from offering a few hints, is the question of how to calculate the transition amplitudes and probability matrix. That is the basic electronic structure part of the problem, which *was* the focus of the original first-principles calculations of angle-resolved photoemission referred to above. I plan to post a couple of supplementary posts in this series; one illustrating the interesting interactions between photon polarisation, electron spin and spin-orbit coupling; the other linking the present general formulation to the underlying electronic structure (described by multiple scattering theory).

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Appendix A Polarisation Basis Vectors

Let the direction of the incident photons point along a unit vector \mathbf{q} with polar angles θ_q, ϕ_q :

$$\mathbf{q} = (\sin\theta_q \cos\phi_q, \sin\theta_q \sin\phi_q, \cos\theta_q)$$

Note that we expect this to be pointing into the crystal, ie we require that $\hat{q}_z < 0$; thus $\pi/2 < \theta_q < \pi$, $\sin\theta_q > 0$, $\cos\theta_q < 0$. To serve as a polarisation basis we need to define a pair of unit vectors $\mathbf{e}^{(1)}, \mathbf{e}^{(2)}$ which are orthogonal to each other and to \mathbf{q} (this latter being a requirement of electrodynamics, not quantum mechanics). We choose $\mathbf{e}^{(1)}$ to lie in the xy-plane of the crystal-fixed Cartesian coordinate system (see section 2), ie in the plane of the surface. This corresponds to s-polarisation in the lingo of photoemission. Finally, we'll take the vector $\mathbf{e}^{(2)}$ to have a positive z-component pointing out of the surface, ie towards the electron detector. This corresponds to p-polarisation in the lingo of photoemission.

To find $\mathbf{e}^{(1)}$, we note that it can be written $\mathbf{e}^{(1)} = (a, b, 0)$, that it must be orthogonal to the photon momentum $\mathbf{e}^{(1)} \cdot \mathbf{q} = 0$ and that it has unit magnitude. This is sufficient to determine $\mathbf{e}^{(1)}$ in terms of the photon polar angles. In fact

$$\mathbf{e}^{(1)} = (\pm \sin\phi_q, \mp \cos\phi_q, 0)$$

To determine the p-polarisation vector, we note that $\mathbf{e}^{(2)} = \mathbf{q} \times \mathbf{e}^{(1)}$, which yields

$$\mathbf{e}^{(2)} = (\pm \cos\theta_q \cos\phi_q, \pm \cos\theta_q \sin\phi_q, \mp \sin\theta_q)$$

But we noted above that the z-component of $\mathbf{e}^{(2)}$ should be positive and that the photon direction was such that $\sin\theta_q > 0$. Thus we choose the lower sign in the above equations for $\mathbf{e}^{(1)}, \mathbf{e}^{(2)}$ and finally write

$$\begin{aligned} \mathbf{q} &= (\sin\theta_q \cos\phi_q, \sin\theta_q \sin\phi_q, \cos\theta_q) \\ \mathbf{e}^{(1)} &= (-\sin\phi_q, \cos\phi_q, 0) \\ \mathbf{e}^{(2)} &= (-\cos\theta_q \cos\phi_q, -\cos\theta_q \sin\phi_q, \sin\theta_q) \end{aligned} \tag{A.6}$$

Now the most general (complex) vector describing a pure polarisation state can be written

$$\boldsymbol{\chi} = \mathbf{e}^{(1)} \cos\alpha + \mathbf{e}^{(2)} \sin\alpha e^{i\beta} \tag{A.7}$$

Why? Because the two coefficients would be complex numbers, but are constrained by unimodularity and the fact that an overall phase is irrelevant – hence we need only 2 real parameters, α, β not 4. If $\beta = 0$ then (A.7) represents linear polarisation at an angle α to $\mathbf{e}^{(1)}$.

If $\alpha = \pi/4$, $\beta = \pm\pi/2$, then (A.7) represents (left/right hand) circular polarisation⁷.

⁷ Note that $(\mathbf{e}^{(1)}, \mathbf{e}^{(2)}, \mathbf{q})$ form a left-handed coordinate system, since we take $\hat{q}_z < 0$ (ie \mathbf{q} points *into* the crystal).

Appendix B Radial and angular parts of the e-photon interaction

The goal here is to give the electron-light interaction in a form convenient for the calculation of matrix elements, including the orbital selection rules, for any experimental geometry. First we write the interaction in terms of the spherical harmonics for $l=1$ (here $\mathbf{r} = r/\|\mathbf{r}\|$ is a unit vector corresponding to the angles θ, ϕ :

$$\begin{aligned} Y_{1-1}(\mathbf{r}) &= \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi} \\ Y_{10}(\mathbf{r}) &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\ Y_{11}(\mathbf{r}) &= -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \end{aligned} \quad (\text{B.1})$$

From these formulae we can easily find

$$\begin{aligned} Y_{1-1}(\mathbf{r}) &= \left(\frac{3}{8\pi}\right)^{1/2} \left(\frac{x-iy}{r}\right) \\ Y_{10}(\mathbf{r}) &= \left(\frac{3}{4\pi}\right)^{1/2} \left(\frac{z}{r}\right) \\ Y_{11}(\mathbf{r}) &= -\left(\frac{3}{8\pi}\right)^{1/2} \left(\frac{x+iy}{r}\right) \end{aligned} \quad (\text{B.2})$$

and

$$\begin{aligned} \frac{x}{r} &= \left(\frac{2\pi}{3}\right)^{1/2} (Y_{1-1}(\mathbf{r}) - Y_{11}(\mathbf{r})) \\ \frac{y}{r} &= \left(\frac{2\pi}{3}\right)^{1/2} i(Y_{1-1}(\mathbf{r}) + Y_{11}(\mathbf{r})) \\ \frac{z}{r} &= \left(\frac{4\pi}{3}\right)^{1/2} Y_{10}(\mathbf{r}) \end{aligned} \quad (\text{B.3})$$

Now if we write

$$\mathbf{e}^{(\lambda)} \cdot \mathbf{r} = r \left(e_x^{(\lambda)} \frac{x}{r} + e_y^{(\lambda)} \frac{y}{r} + e_z^{(\lambda)} \frac{z}{r} \right)$$

and use (B.3), then it's algebra to show that

$$\mathbf{e}^{(\lambda)} \cdot \mathbf{r} = \left(\frac{4\pi}{3}\right)^{1/2} r \sum_{m=-1}^1 g_m^{(\lambda)} Y_{1m}(\mathbf{r}) \quad (\text{B.4})$$

where the coefficients are given by

$$\begin{aligned}
g_{-1}^{(\lambda)} &= \frac{e_x^{(\lambda)} + ie_y^{(\lambda)}}{\sqrt{2}} \\
g_0^{(\lambda)} &= e_z^{(\lambda)} \\
g_1^{(\lambda)} &= -\frac{e_x^{(\lambda)} - ie_y^{(\lambda)}}{\sqrt{2}}
\end{aligned} \tag{B.5}$$

Being combinations of the photon polarisation vector components given by (A.6), these coefficients are functions of the photon incidence angles. [Note that this little piece of algebra is an illustration of the theory of spherical tensor operators (here tensors of rank 1, ie vectors) using explicit formulae for the spherical harmonics. It's an easy application, obviously, so there seems no need to use the full tensor operator machinery, Wigner-Eckart theorem [4] etc, even though that's actually what's going on here.]

Finally, we note that there's no dependence on spin in this interaction. Thus, just to be formal about it and write the interaction as an operator in the tensor product space of orbital and spin degrees of freedom, the spin operator is the unit operator:

$$\mathcal{V}^{(\lambda)} = \mathcal{V}^{(\lambda)} \otimes \mathbf{1} \tag{B.6}$$

Here the "orbital" part of the operator is given by

$$\begin{aligned}
\langle \mathbf{r} | \mathcal{V}^{(\lambda)} | \mathbf{r}' \rangle &= \mathcal{V}^{(\lambda)}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \\
\mathcal{V}^{(\lambda)}(\mathbf{r}) &= -e\mathcal{E} \mathbf{e}^{(\lambda)} \cdot \mathbf{r} = -e\mathcal{E} \left(\frac{4\pi}{3} \right)^{1/2} r \sum_{m=-1}^1 g_m^{(\lambda)}(\mathbf{q}) Y_{1m}(\mathbf{r})
\end{aligned} \tag{B.7}$$

In this last equation we noted explicitly that the g-factors are functions of the photon direction through the polarisation vectors $\mathbf{e}^{(1)}, \mathbf{e}^{(2)}$.

Appendix C Projectors in a continuous state space

Projection operators in a discrete state space are pretty simple objects, but, as the present application to photoemission demonstrates, projectors in a continuous space, (6.1) for instance, are a bit more tricky, liable to lead the naïve into puzzling formulae involving dangling delta functions and similar dangerous-looking algebra. In this appendix, we give some results which are needed in the photoemission problem and illustrate how to deal with such continuous space problems.

Let's define a projector in momentum space by a slightly modified version of (6.1):

$$\begin{aligned} \mathcal{P}(\mathbf{k}) &= \int_{\mathbf{k}-\Delta\mathbf{k}/2}^{\mathbf{k}+\Delta\mathbf{k}/2} d\mathbf{k}' |\mathbf{k}'\rangle \langle \mathbf{k}'| \\ &\equiv \int_{k_x-\Delta k_x/2}^{k_x+\Delta k_x/2} dk'_x |k'_x\rangle \langle k'_x| \otimes \int_{k_y-\Delta k_y/2}^{k_y+\Delta k_y/2} dk'_y |k'_y\rangle \langle k'_y| \otimes \int_{k_z-\Delta k_z/2}^{k_z+\Delta k_z/2} dk'_z |k'_z\rangle \langle k'_z| \end{aligned} \quad (\text{C.1})$$

Let's define a shorthand notation

$$\mathbf{k}^{(\pm)} = \left(k_x^{(\pm)}, k_y^{(\pm)}, k_z^{(\pm)} \right) \equiv \left(k_x \pm \Delta k_x / 2, k_y \pm \Delta k_y / 2, k_z \pm \Delta k_z / 2 \right) \quad (\text{C.2})$$

Then (C.1) becomes

$$\mathcal{P}(\mathbf{k}) = \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}' |\mathbf{k}'\rangle \langle \mathbf{k}'| \quad (\text{C.3})$$

Here we have omitted (for now; we'll put them back at the end) the irrelevant spin degrees of freedom – they are discrete and cause no problems – and written the momentum integral in terms of Cartesian, rather than polar, coordinates. The point is that (C.1) projects on to a region of momentum space centred on \mathbf{k} and with volume $\Omega = \Delta k_x \Delta k_y \Delta k_z$. We imagine that this volume is small, representing something like the resolution of a measuring apparatus, but not zero.

Note that we can always write

$$\int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}' f(\mathbf{k}') = \int_{-\infty}^{\infty} d\mathbf{k}' \theta(\mathbf{k}' - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \mathbf{k}') f(\mathbf{k}') \quad (\text{C.4})$$

where $\theta(x)$ is the Heavyside function:

$$\begin{aligned} \theta(x) &= \begin{cases} 0 & \text{for } x < 0 \\ 1 & \text{for } x \geq 0 \end{cases} \\ \theta(x)^2 &= \theta(x) \\ \theta(\mathbf{x}) &\equiv \theta(x) \otimes \theta(y) \otimes \theta(z) \end{aligned} \quad (\text{C.5})$$

Now consider a matrix element between arbitrary kets $|\psi\rangle, |\psi'\rangle$:

$$\langle \psi | \mathcal{P}(\mathbf{k}) | \psi' \rangle = \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}' \langle \psi | \mathbf{k}' \rangle \langle \mathbf{k}' | \psi' \rangle$$

If Ω (let's call it the resolution volume) is small enough, and if the amplitudes $\langle \psi | \mathbf{k}' \rangle, \langle \mathbf{k}' | \psi' \rangle$ are smooth functions of \mathbf{k}' , then it will be a good approximation to set them equal to $\langle \psi | \mathbf{k} \rangle, \langle \mathbf{k} | \psi' \rangle$ and take them out of the integral, which is then trivial:

$$\langle \psi | \mathcal{P}(\mathbf{k}) | \psi' \rangle \approx \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle \Omega \quad (\text{C.6})$$

This is very sensible physically. If the resolution becomes infinitely small, $\Omega \rightarrow 0$ (the size of the pinhole or whatever in the apparatus goes to zero), then the amplitude for a particle to get through must also go to zero, linearly. But it would be a mistake to assume that $\Omega \rightarrow 0$ is equivalent to $\mathcal{P}(\mathbf{k}) \rightarrow |\mathbf{k}\rangle\langle\mathbf{k}|$, because that would produce the result $\langle\psi|\mathcal{P}(\mathbf{k})|\psi'\rangle \simeq \langle\psi|\mathbf{k}\rangle\langle\mathbf{k}|\psi'\rangle$.

In the same vein, let's consider the matrix element $\langle\psi|\mathcal{P}(\mathbf{k})\mathcal{P}(\mathbf{k})|\psi'\rangle$. Taking the amplitudes outside the integral, as above, leads to

$$\begin{aligned}\langle\psi|\mathcal{P}(\mathbf{k})\mathcal{P}(\mathbf{k})|\psi'\rangle &= \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_1 \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_2 \langle\psi|\mathbf{k}_1\rangle\langle\mathbf{k}_1|\mathbf{k}_2\rangle\langle\mathbf{k}_2|\psi'\rangle \\ &\simeq \langle\psi|\mathbf{k}\rangle\langle\mathbf{k}|\psi'\rangle \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_1 \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_2 \langle\mathbf{k}_1|\mathbf{k}_2\rangle\end{aligned}\quad (\text{C.7})$$

But this time the remaining double integral does not look so trivial. Clearly it is a product of 3 1-dimensional integrals of the form

$$I(k_x, \Delta k_x) \equiv \int_{k_x^{(-)}}^{k_x^{(+)}} dk_1 \int_{k_x^{(-)}}^{k_x^{(+)}} dk_2 \langle k_1 | k_2 \rangle$$

Now we can proceed, using (C.4) and (C.5), as follows:

$$\begin{aligned}I(k_x, \Delta k_x) &= \int_{k_x^{(-)}}^{k_x^{(+)}} dk_1 \int_{-\infty}^{\infty} dk_2 \theta(k_2 - k_x^{(-)}) \theta(k_x^{(+)} - k_2) \delta(k_1 - k_2) \\ &= \int_{k_x^{(-)}}^{k_x^{(+)}} dk_1 \theta(k_1 - k_x^{(-)}) \theta(k_x^{(+)} - k_1) = \Delta k_x\end{aligned}$$

Reverting back to 3 dimensions, we can now see that

$$\int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_1 \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_2 \langle\mathbf{k}_1|\mathbf{k}_2\rangle = \Delta_x \Delta_y \Delta_z = \Omega \quad (\text{C.8})$$

and (C.7) becomes

$$\langle\psi|\mathcal{P}(\mathbf{k})\mathcal{P}(\mathbf{k})|\psi'\rangle \simeq \langle\psi|\mathbf{k}\rangle\langle\mathbf{k}|\psi'\rangle \Omega \quad (\text{C.9})$$

Next consider the matrix element $\langle\mathbf{k}'|\mathcal{P}(\mathbf{k})|\psi\rangle$, where, again, $|\psi\rangle$ is some arbitrary state ket. Then, proceeding as above,

$$\begin{aligned}\langle\mathbf{k}'|\mathcal{P}(\mathbf{k})|\psi\rangle &= \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\bar{\mathbf{k}} \langle\mathbf{k}'|\bar{\mathbf{k}}\rangle\langle\bar{\mathbf{k}}|\psi\rangle \\ &\simeq \langle\mathbf{k}'|\psi\rangle \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\bar{\mathbf{k}} \langle\mathbf{k}'|\bar{\mathbf{k}}\rangle = \langle\mathbf{k}'|\psi\rangle \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\bar{\mathbf{k}} \delta(\bar{\mathbf{k}} - \mathbf{k}')\end{aligned}\quad (\text{C.10})$$

But now we can use (C.4) to write

$$\int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\bar{\mathbf{k}} \delta(\bar{\mathbf{k}} - \mathbf{k}') = \int_{-\infty}^{\infty} d\bar{\mathbf{k}} \theta(\bar{\mathbf{k}} - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \bar{\mathbf{k}}) \delta(\bar{\mathbf{k}} - \mathbf{k}') = \theta(\mathbf{k}' - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \mathbf{k}')$$

Thus

$$\langle\mathbf{k}'|\mathcal{P}(\mathbf{k})|\psi\rangle = \langle\mathbf{k}'|\psi\rangle \theta(\mathbf{k}' - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \mathbf{k}') \quad (\text{C.11})$$

Note that (C.11) implies

$$\begin{aligned}
\int_{-\infty}^{\infty} d\mathbf{k}' \langle \psi | \mathcal{P}(\mathbf{k}) | \mathbf{k}' \rangle \langle \mathbf{k}' | \mathcal{P}(\mathbf{k}) | \psi' \rangle &= \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle \int_{-\infty}^{\infty} d\mathbf{k}' \theta(\mathbf{k}' - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \mathbf{k}') \theta(\mathbf{k}' - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \mathbf{k}') \\
&= \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle \int_{-\infty}^{\infty} d\mathbf{k}' \theta(\mathbf{k}' - \mathbf{k}^{(-)}) \theta(\mathbf{k}^{(+)} - \mathbf{k}') \\
&= \Omega \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle
\end{aligned}$$

Of course, this must be the case for (C.11) to be consistent with (C.9), so all is well.

Now consider the following matrix element of some operator \mathcal{A} :

$$\begin{aligned}
\langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k}) | \psi' \rangle &= \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_1 \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_2 \langle \psi | \mathbf{k}_1 \rangle \langle \mathbf{k}_1 | \mathcal{A} | \mathbf{k}_2 \rangle \langle \mathbf{k}_2 | \psi' \rangle \\
&\simeq \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_1 \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_2 \langle \mathbf{k}_1 | \mathcal{A} | \mathbf{k}_2 \rangle
\end{aligned}$$

Depending on \mathcal{A} , it may be OK to make the further approximation

$$\langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k}) | \psi' \rangle \simeq \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle \langle \mathbf{k} | \mathcal{A} | \mathbf{k} \rangle$$

But note that if \mathcal{A} happens to be a function $f(\mathbf{p})$ of the momentum operator \mathbf{p} , then

$\langle \mathbf{k}_1 | \mathcal{A} | \mathbf{k}_2 \rangle = f(\mathbf{k}_1) \langle \mathbf{k}_1 | \mathbf{k}_2 \rangle$, and we have the same problem considered above. If the function f is smooth, we can write, using (C.8)

$$\begin{aligned}
\langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k}) | \psi' \rangle &= \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle f(\mathbf{k}) \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_1 \int_{\mathbf{k}^{(-)}}^{\mathbf{k}^{(+)}} d\mathbf{k}_2 \langle \mathbf{k}_1 | \mathbf{k}_2 \rangle \\
&\simeq \langle \psi | \mathbf{k} \rangle \langle \mathbf{k} | \psi' \rangle f(\mathbf{k}) \Omega
\end{aligned} \tag{C.12}$$

Note that if \mathcal{A} is independent of momentum, then $f(\mathbf{k})=1$ and we regain (C.9).

Formulas (C.6), (C.9) and (C.12) are all we need for the photoemission problem. Putting the spin in again, as per (6.1), we obtain

$$\begin{aligned}
\langle \psi | \mathcal{P}(\mathbf{k}) | \psi' \rangle &= \Omega \sum_m \langle \psi | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \psi' \rangle = \langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{P}(\mathbf{k}) | \psi' \rangle \\
\langle \mathbf{k}', m | \mathcal{P}(\mathbf{k}) | \psi \rangle &= \langle \mathbf{k}, m | \psi \rangle \theta(\mathbf{k}' - \mathbf{k}_-) \theta(\mathbf{k}_+ - \mathbf{k}')
\end{aligned} \tag{C.13}$$

And for the two cases in which $\mathcal{A} = f(\mathbf{p}) \otimes \mathbf{1}_s$, ie independent of spin, or $\mathcal{A} = g(s) \otimes \mathbf{1}_k$, ie independent of momentum, we get

$$\begin{aligned}
\langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k}) | \psi' \rangle &= \Omega f(k) \sum_m \langle \psi | \mathbf{k}, m \rangle \langle \mathbf{k}, m | \psi' \rangle && \text{if } \mathcal{A} = f(\mathbf{p}) \otimes \mathbf{1}_s \\
\langle \psi | \mathcal{P}(\mathbf{k}) \mathcal{A} \mathcal{P}(\mathbf{k}) | \psi' \rangle &= \Omega \sum_m \langle \psi | \mathbf{k}, m \rangle \langle m_1 | g(s) | m_2 \rangle \langle \mathbf{k}, m | \psi' \rangle && \text{if } \mathcal{A} = g(s) \otimes \mathbf{1}_k
\end{aligned} \tag{C.14}$$