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Angular correlation patterns in double Auger decay

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Abstract

The angular distribution of two emitted electrons in the double Auger process in atoms has been theoretically investigated. In particular, the double Auger decay of a 1s vacancy in Ne and a 2p vacancy in Ar is considered. In analogy with double photoionization, we present a convenient parametrization of the angular correlation patterns for all possible angular momenta of the emitted electron pair. As a limiting case we investigate the angular correlations within the shake-off mechanism of the double Auger process. We also consider the influence of initial orientation of the vacancy on the electron angular distributions (circular dichroism).

1. Introduction

When an inner-shell vacancy is produced in a light atom, for example, by photoionization, its relaxation usually occurs via an Auger transition—a radiationless process in which one of the outer electrons fills the vacancy and another is ejected with energy equal to the transition energy. However, in some cases (5–20% of all transitions) two electrons are simultaneously emitted, sharing the transition energy. This process is usually referred to as a double Auger (DA) decay. In resonant Auger decay the similar process is often called 'shake-off' indicating one of the possible mechanisms of two-electron emission. Because the Coulomb operator responsible for the Auger decay is a two-particle operator, DA decay is forbidden within the independent particle model (frozen atomic structure approximation). Its occurrence, therefore, is a consequence of electron–electron correlations, and the study of DA decay may be used as a testing ground for theoretical models which incorporate such correlations. A similar goal is pursued in studying another process with two-electron emission—the double photoionization (DPI) process. In this context, the advantage of DA decay is that a broader variety of two-electron continuum quantum numbers is available in the DA transition. In comparison, DPI is restricted by the dipole selection rules.

The first experimental evidence for a DA process was reported by Carlson and Krause (1965) for the K–LLL transition in Ne. Since then the DA process in ions and the analogous

resonant DA process in atoms (resonant shake-off) have been studied by various experimental techniques: photoelectron spectroscopy (Carlson and Krause 1966, Becker *et al* 1986, 1989, Heimann *et al* 1987), multiply-charged photoion yield measurements (Ueda *et al* 1991), photoion–Auger-electron coincidence measurements (Levin *et al* 1990, Tamenory *et al* 2002 and references therein), the photoelectron–ion coincidence method (Kämmerling *et al* 1992, Kanngießer *et al* 2000, Brünken *et al* 2002 and references therein). All these experiments concern the total probability of the DA decay, and most measurements deduce the probability only indirectly, mainly from the charge distribution of the photoions. Only quite recently first coincidence measurements of the two emitted electrons were reported for DA decay induced by K-capture (Hindi *et al* 1996) and by photoionization (Viefhaus *et al* 2002, 2004, Viefhaus 2003). Such measurements are much more informative since not only the total yield, but also the energy sharing (Hindi *et al* 1996, Viefhaus *et al* 2002) and even the angular correlations between emitted electrons (Viefhaus *et al* 2004) are measured.

Theoretically, mainly total probability was considered within the shake-off model based on the sudden perturbation approach (Carlson and Krause 1965, Krause and Carlson 1967, Parilis 1969, Kochur *et al* 1995). More refined calculations within many-body perturbation theory (MBPT) including calculations of the energy-sharing distribution were only done for the DA transitions in Ne $1s^{-1} \rightarrow 2s^{-2}2p^{-1}$ (Amusia *et al* 1992) and Kr $3d^{-1} \rightarrow 4s^{-1}4p^{-2}$ (Kilin *et al* 1997) as well as for the resonant DA transitions from the Kr $3d^{-1}5p$ resonance (Amusia *et al* 1993). A special problem of post-collision interaction in the DA process was treated theoretically by Sheinerman (1998). To the best of our knowledge, the angular correlations between two emitted electrons in the DA process have only been calculated by Amusia *et al* (1992) for the Ne $1s^{-1} \rightarrow 2s^{-2}2p^{-1}$ transition.

In the present paper, we consider theoretically the general properties of the angular distributions of Auger electrons emitted in DA decay. Our work was stimulated to a great extent by the development in theoretical analysis of angular correlations between two electrons in DPI. Here two directions of theoretical investigations are clearly distinguished (see, for example, the review by Briggs and Schmidt (2000)). On one hand, there are *ab initio* calculations of triple-differential cross sections (TDCS) within elaborate theoretical models (see, e.g., Kheifets and Bray (2002) and Kazansky *et al* (2003) and references therein), but on the other hand, a very useful parametrization of the DPI amplitude and the TDCS has been suggested (Huetz *et al* 1991, Malegat *et al* 1997, Cvejanović and Reddish 2000). The usefulness of the parametrization is due to the fact that there is a great variety of angular correlation patterns measured in different experimental geometries which in fact can be all described by a small number of parameters (complex gerade and ungerade amplitudes). Moreover, these parameters are only slowly varying functions of the photon energy, which makes it easy to compare the experimental data obtained by different groups at different energies. The main goal of our work is to work out a similar parametrization for the angular correlations in DA decay. Based on the experience with the DPI studies we hope that such parametrization will be useful for the analysis of the experimental data as well as for the planning of new experiments.

2. General expression and parametrization for the angular distribution of two emitted Auger electrons

2.1. Derivation of the basic formulae

The theory of DA decay is based on a two-step model, where direct triple photoionization is negligible and the amplitude of the process is treated as a product of the hole-creation and DA decay amplitudes. In this model, a general expression for the angular distribution of two

Auger electrons emitted in DA decay has been derived by Amusia *et al* (1992) within the framework of the density matrix and statistical tensor formalism (see, e.g., Blum (1996) and Balashov *et al* (2000)). However, this expression is rather complicated and it can hardly be used for the analysis of experimental data without detailed and laborious calculations. Below, we re-derive the general expression in a form which allows a simple parametrization. We start from the decay of an unpolarized ionic state with an inner-shell vacancy (influence of vacancy polarization will be discussed in section 3). In the following, we use an *LS*-coupling approximation which is appropriate for light and medium atoms. A double Auger transition from the initial $|\alpha_i L_i S_i\rangle$ state to the final $|\alpha_f L_f S_f\rangle$ state with emission of two electrons with momenta $\mathbf{k_1}$ and $\mathbf{k_2}$ and spin projections μ_1 and μ_2 is described by the Auger amplitude

$$\mathcal{M}_{M_{L_i} M_{L_f}} = \langle \alpha_f L_f M_{L_f} S_f M_{S_f}, \mathbf{k_1}\mu_1, \mathbf{k_2}\mu_2 | V | \alpha_i L_i M_{L_i} S_i M_{S_i} \rangle, \tag{1}$$

where V is a Coulomb operator, M_L and M_S are the projections of the corresponding angular momenta and α_i and α_f denote all other quantum numbers which are necessary to specify the state. Expanding the electron wavefunctions in partial waves and coupling the orbital angular momenta and spins of the emitted electrons in the total orbital angular momentum (L) and total spin (S) of the electron pair, respectively, we get

$$\begin{aligned}\mathcal{M}_{M_{L_i} M_{L_f}} = {} & \sum_S \xi^S(\mu_1\mu_2 M_{S_f}; M_{S_i}) \sum_{\ell_1\ell_2 L M_L} \left(L_f M_{L_f}, L M_L | L_i M_{L_i}\right) \\ & \times Y^{\ell_1,\ell_2}_{L M_L}(\mathbf{n_1}, \mathbf{n_2}) \hat{L}_i^{-1} \langle \alpha_f L_f, (\varepsilon_1\ell_1, \varepsilon_2\ell_2) L \| V^S \| \alpha_i L_i \rangle,\end{aligned} \tag{2}$$

where $\mathbf{n_1}$ and $\mathbf{n_2}$ are the unit vectors in the directions $\mathbf{k_1}$ and $\mathbf{k_2}$, respectively, ε_1 and ε_2 are the energies of the emitted electrons, ℓ_1 and ℓ_2 are their orbital angular momenta, $\hat{L} \equiv (2L+1)^{1/2}$, $\left(L_f M_{L_f}, L M_L | L_i M_{L_i}\right)$ is a Clebsch–Gordan coefficient and

$$Y^{\ell_1,\ell_2}_{L M_L}(\mathbf{n_1}, \mathbf{n_2}) = \sum_{m_1,m_2} (\ell_1 m_1, \ell_2 m_2 | L M_L) Y_{\ell_1 m_1}(\mathbf{n_1}) Y_{\ell_2 m_2}(\mathbf{n_2}), \tag{3}$$

are the bipolar harmonics (Varshalovich *et al* 1988). Since the Coulomb operator V does not contain spin, the spin part of the matrix element (1) is separated in the factor

$$\begin{aligned}\xi^S(\mu_1\mu_2 M_{S_f}; M_{S_i}) = {} & \sum_{M_S} \left(\tfrac{1}{2}\mu_1, \tfrac{1}{2}\mu_2 | S M_S\right) \left(S_f M_{S_f}, S M_S | S_i M_{S_i}\right) \\ & \times \left\langle S_f, \left(\tfrac{1}{2}\tfrac{1}{2}\right) S : S_i M_{S_i} \middle| I \middle| S_i M_{S_i} \right\rangle,\end{aligned} \tag{4}$$

where I is a unit operator. The reduced matrix element in (2) still depends on S since the symmetry of the orbital part of the two-electron wavefunction depends on S (in general, coefficients of fractional parentage depending on S may also be included in this matrix element).

The probability of emitting two electrons in the directions $\mathbf{n_1}$ and $\mathbf{n_2}$ can be written as

$$\frac{\mathrm{d}W}{\mathrm{d}\varepsilon_1\, \mathrm{d}\mathbf{n_1}\, \mathrm{d}\mathbf{n_2}} = 2\pi \hat{L}_i^{-2} \hat{S}_i^{-2} \sum_{M_{L_i} M_{S_i}} \sum_{\substack{M_{L_f} M_{S_f} \\ \mu_1\mu_2}} \left| \mathcal{M}_{M_{L_i} M_{L_f}} \right|^2. \tag{5}$$

Substituting the amplitude (2) into (5) and summing over projections of angular momenta and spins we get

$$\frac{\mathrm{d}W}{\mathrm{d}\varepsilon_1\, \mathrm{d}\mathbf{n_1}\, \mathrm{d}\mathbf{n_2}} = 2\pi \hat{L}_i^{-2} \hat{S}_i^{-2} \sum_{SL} F_{SL}, \tag{6}$$

where

$$F_{SL} = \sum_{M_L} \left| f_{SLM_L} \right|^2 , \tag{7}$$

$$f_{SLM_L} = \hat{L}^{-1} \sum_{\ell_1 \ell_2} Y_{LM_L}^{\ell_1,\ell_2}(\mathbf{n_1}, \mathbf{n_2}) \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) L \| V^S \| \alpha_i L_i \rangle . \tag{8}$$

The probability (6) is a sum of partial probabilities F_{SL} corresponding to different terms LS of the outgoing pair of Auger electrons.

According to the selection rules for the Coulomb operator, the orbital angular momentum L and parity $\pi = (-1)^{\ell_1+\ell_2}$ of the emitted electron pair are restricted by the conditions

$$|L_i - L_f| \leqslant L \leqslant L_i + L_f, \qquad \pi = \pi_i \pi_f , \tag{9}$$

where π_i and π_f are the parities of the initial and final ionic states, respectively. Besides, $S = 0$ or 1. Restrictions (9) limit the number of terms in sum (6). Since the total wavefunction of the final state of the emitted pair should be antisymmetric with respect to a permutation of the two electrons, the matrix elements should satisfy the relation

$$\langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) L \| V^S \| \alpha_i L_i \rangle = (-1)^{\pi+L+S} \langle \alpha_f L_f, (\varepsilon_2 \ell_2, \varepsilon_1 \ell_1) L \| V^S \| \alpha_i L_i \rangle . \tag{10}$$

Equation (6) is bilinear in bipolar harmonics and therefore is impractical for parametrization of the angular correlation function. To proceed further we use an elegant method suggested recently by Manakov *et al* (1996) which allows reduction of bipolar harmonics of higher ranks of internal spherical functions by expressing them in terms of 'minimal' harmonics. (A similar reduction has been given independently by Malegat *et al* (1997).) Using this method one can obtain a convenient parametrization of the amplitudes (8). Summing over M_L analytically in equation (7), one obtains the probabilities F_{SL} for any $LS\pi$ final state of the emitted electrons.

Consider, for example, emission of Auger electrons in a $^{2S+1}\mathrm{P^o}$ state. The amplitude (8) in this case takes the form

$$f_{S1M} = (\sqrt{3})^{-1} \sum_{\ell_1 \ell_2} Y_{1M}^{\ell_1,\ell_2}(\mathbf{n_1}, \mathbf{n_2}) \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) \mathrm{P^o} \| V^S \| \alpha_i L_i \rangle . \tag{11}$$

Due to parity selection rule, only $\ell_2 = \ell_1 \pm 1$ contribute to the sum in (11). The bipolar harmonic in this equation can be reduced to the form (see equation (C.2) of Manakov *et al* (1996))

$$Y_{1M}^{\ell_1,\ell_2}(\mathbf{n_1}, \mathbf{n_2}) = -\frac{1}{4\pi} \sqrt{\frac{3}{\ell_{\max}}} \left[(-1)^{\ell_1} P_{\ell_1}^{(1)}(\cos\theta_{12}) n_{1M} + (-1)^{\ell_2} P_{\ell_2}^{(1)}(\cos\theta_{12}) n_{2M} \right]. \tag{12}$$

Here and below $P_\ell^{(k)}(x) = \mathrm{d}^k P_\ell(x)/\mathrm{d}x^k$, where $P_\ell(x)$ is the Legendre polynomial; θ_{12} is the angle between the two emission directions and n_{1M} and n_{2M} ($M = 0, \pm 1$) are the spherical components of the unit vectors $\mathbf{n_1}$ and $\mathbf{n_2}$. Introducing the amplitudes

$$b_j^S(\theta_{12}) = \frac{1}{4\pi} \sum_{\ell_1 \ell_2} \frac{1}{\sqrt{\ell_{\max}}} (-1)^{\ell_j+1} P_{\ell_j}^{(1)}(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) \mathrm{P^o} \| V^S \| \alpha_i L_i \rangle , \qquad j = 1, 2, \tag{13}$$

where $\ell_{\max} = \max\{\ell_1, \ell_2\}$, we can present f_{S1M}, equation (11), as

$$f_{S1M} = b_1^S(\theta_{12}) n_{1M} + b_2^S(\theta_{12}) n_{2M} , \tag{14}$$

and the corresponding probability (7) as

$$F_{S\mathrm{P^o}} = \sum_M |f_{S1M}|^2 = |b_1|^2 + |b_2|^2 + 2\mathrm{Re}\big[b_1^S b_2^{S*}(\mathbf{n_1}\cdot\mathbf{n_2})\big]. \tag{15}$$

We omit the argument θ_{12} in the amplitudes for brevity.

As follows from (10), a permutation of the two electrons leads to the relation $b_1^S(2,1) = (-1)^S b_2^S(1,2)$. In analogy with the DPI (Huetz *et al* 1991, Briggs and Schmidt 2000) it is convenient to introduce combinations of the amplitudes gerade $\left(a_{\mathrm{g}}^S\right)$ and ungerade $\left(a_{\mathrm{u}}^S\right)$ with respect to the permutations:

$$a_{\mathrm{g}}^S = \tfrac{1}{\sqrt{2}}\big(b_1^S + (-1)^S b_2^S\big), \qquad a_{\mathrm{u}}^S = \tfrac{1}{\sqrt{2}}\big(b_1^S - (-1)^S b_2^S\big). \tag{16}$$

From (15) and (16) we obtain for the angular correlation function in the $^{2S+1}\mathrm{P^o}$ states of the outgoing electron pair

$$F_{S\mathrm{P^o}} = \left|a_{\mathrm{g}}^S\right|^2(1 + (-1)^S\cos\theta_{12}) + \left|a_{\mathrm{u}}^S\right|^2(1 - (-1)^S\cos\theta_{12}), \qquad S = 0, 1. \tag{17}$$

In the same way, expressions for the probability of emission F_{SL} for other $LS\pi$ can be obtained. The results are presented in table 1 for $L \leqslant 3$ with the corresponding amplitudes listed in the appendix.

Let us discuss the obtained results using the $^{2S+1}\mathrm{P^o}$ case (17) as an example. First, we note that all probabilities depend only on the relative angle of two-electron emission as it should be since the initial ionic state is unpolarized. It is easy to check that all kinematical selection rules (A)–(I) of Maulbetsch and Briggs (1995), pertinent to the process leading to a two-electron continuum state, are fulfilled. For example, selection rule (C) claims that for $\mathbf{k}_1 = -\mathbf{k}_2$ states with $(\pi + S)$ *odd* do not contribute to the process. Indeed, in this case $\varepsilon_1 = \varepsilon_2$, hence $a_{\mathrm{u}}^S = 0$ and, as follows from (17), at $\theta_{12} = 180^\circ$ (back-to-back emission) only $S = 1$ contributes. Similarly, selection rule (D), claiming that for $\mathbf{k}_1 = \mathbf{k}_2$ *triplet* states do not contribute to the process, is obviously fulfilled in the case of equation (17) and all other cases from table 1. It is significant that the validity of the all kinematical selection rules of Maulbetsch and Briggs is provided not by the amplitudes a_{g}^S and a_{u}^S but by the kinematical factors in complete analogy with the DPI (see, e.g., Briggs and Schmidt (2000)). As in the latter case, the amplitudes a_{g}^S and a_{u}^S describe the dynamics of the electron–electron correlations and the squares $\left|a_{\mathrm{g}}^S\right|^2$ and $\left|a_{\mathrm{u}}^S\right|^2$ may be called the correlation factors. This separation into kinematical and dynamical factors in DA process is not so obvious as in DPI, since both factors depend on one and the same angle θ_{12}, the relative angle of the emission of two Auger electrons. (We recall that in DPI the kinematical factor depends on the angles between the emission directions and the photon polarization.) Nevertheless, a similarity of the experimental angular correlation patterns observed for DA decay (Viefhaus *et al* 2004) and for the DPI of He strongly supports the interpretation of the values $\left|a_{\mathrm{g}}^S\right|^2$ and $\left|a_{\mathrm{u}}^S\right|^2$ as the correlation factors determined mainly by the interaction of the two continuum electrons.

As is well known, in DPI the correlation factor primarily reflects the electron–electron repulsion; it should have a maximum at $\theta_{12} = 180^\circ$ (electrons emerge in opposite directions) and vanish at $\theta_{12} = 0$ (electrons emerge in the same direction). From fits to numerous experimental DPI data and partly from theoretical considerations it has been shown that the correlation factor may be accurately approximated by a Gaussian function (see Briggs and Schmidt (2000) and Cvejanović and Reddish (2000) for a review of the data up to 2000 and Kheifets and Bray (2002) for more recent results):

$$C(\theta_{12}) \approx a\exp\left(-4\ln 2(\theta_{12} - 180^\circ)^2/\theta_0^2\right). \tag{18}$$

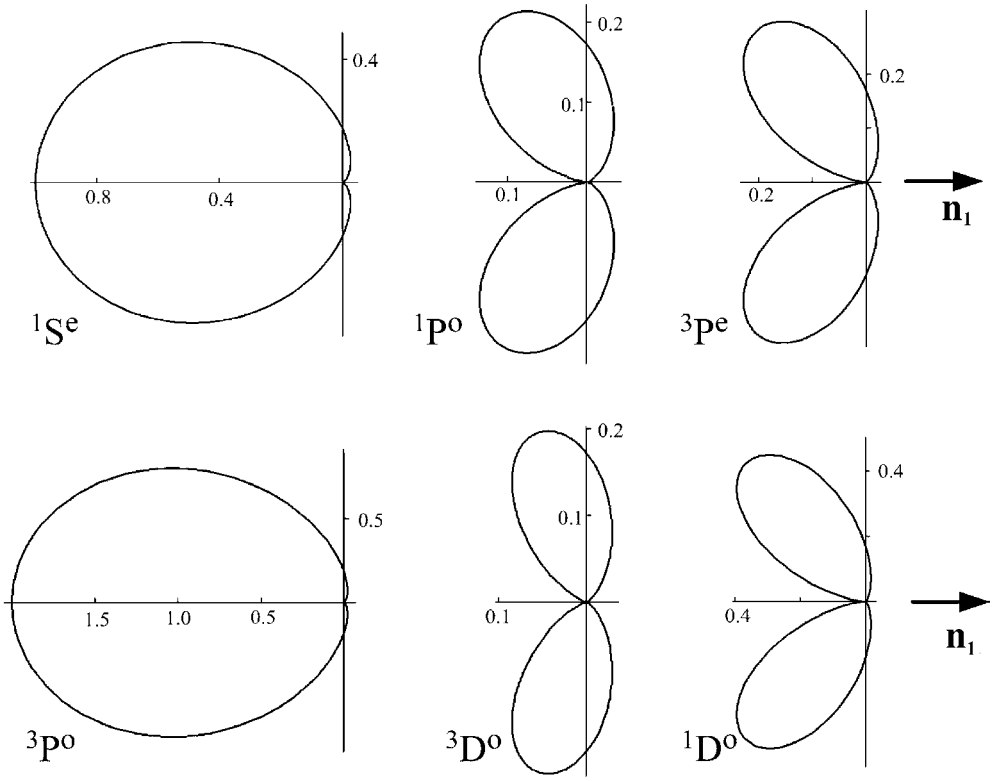

Figure 1. General patterns for the angular distribution of the second electron in the DA process when the direction of emission of the first electron $\mathbf{n_1}$ is fixed, for different $LS\pi$-symmetries of the emitted pair. The case $\varepsilon_1 = \varepsilon_2$ is chosen (see the text).

The parameters of the distribution, the strength a and the full-width at half-maximum θ_0, depend only on the electrons' energy. The behaviour of the parameters as a function of the total energy of the two electrons and energy sharing is rather well known at least in DPI of He (Cvejanović and Reddish 2000). Because of the similarity of angular distributions for DPI and DA decay, as a first attempt it is reasonable to also use similar parametrization for the correlation factors in the DA process. In figure 1 we show the calculated angular patterns for DA decay for various $LS\pi$ calculated for equal energy sharing of two emitted Auger electrons. The correlation factor $\left|a_{\mathrm{g}}^{S}\right|^2$ was approximated by the Gaussian function (18) with the width $\theta_0 = 113^\circ$ and the strength $a = 1$ for all $LS\pi$ symmetries. This value of θ_0 was taken as in Viefhaus *et al* (2004) from empirical interpolation based on fitting all available He DPI data at different dynamical conditions to the energy of 163 eV, equally shared between the outgoing electrons (Cvejanović 2003). The energy of 163 eV corresponds to the double Auger decay of the $2p^{-1}\,{}^2P^o$ vacancy in Ar to the $3p^{-3}$ configuration. As seen from the figure, both kinematical and correlation factors are important in producing the angular correlation pattern. For example, in the case of ${}^1P^o$ emission (see equation (17)), zero at $\theta_{12} = 180^\circ$ is determined by the kinematical factor, while zero at $\theta_{12} = 0$ is due to the correlation factor (Coulomb repulsion). As is clear from symmetry considerations, all patterns are symmetric with respect to transformation $\theta_{12} \to -\theta_{12}$.

Table 1. Parametrization of the angular correlation patterns for DA emission for different symmetries $LS\pi$ of double electron continuum. Corresponding expressions for $a_{\rm g}^S$ and $a_{\rm u}^S$ are given in the appendix.

State	Angular correlation function F_{SL}
$^{1,3}\mathrm{S^e}$	$\left\|a_{\rm g}^S\right\|^2 \delta_{S0} + \left\|a_{\rm u}^S\right\|^2 \delta_{S1}$
$^{1,3}\mathrm{P^o}$	$\left\|a_{\rm g}^S\right\|^2 (1 + (-1)^S \cos\theta_{12}) + \left\|a_{\rm u}^S\right\|^2 (1 - (-1)^S \cos\theta_{12})$
$^{1,3}\mathrm{P^e}$	$\left[\left\|a_{\rm g}^S\right\|^2 \delta_{S1} + \left\|a_{\rm u}^S\right\|^2 \delta_{S0}\right] \sin^2\theta_{12}$
$^{1,3}\mathrm{D^o}$	$\left[\left\|a_{\rm g}^S\right\|^2 (1 - (-1)^S \cos\theta_{12}) + \left\|a_{\rm u}^S\right\|^2 (1 + (-1)^S \cos\theta_{12})\right] \sin^2\theta_{12}$
$^{1,3}\mathrm{D^e}$	$\frac{1}{2}\left(\left\|a_{1\rm g}^S\right\|^2 \delta_{S0} + \left\|a_{1\rm u}^S\right\|^2 \delta_{S1}\right) + \frac{2}{3}\left(\left\|a_{3\rm g}^S\right\|^2 + \left\|a_{3\rm u}^S\right\|^2\right) - \frac{1}{3}(-1)^S\left(\left\|a_{3\rm g}^S\right\|^2 - \left\|a_{3\rm u}^S\right\|^2\right)$
	$+\left[\frac{1}{6}\left(\left\|a_{1\rm g}^S\right\|^2 \delta_{S0} + \left\|a_{1\rm u}^S\right\|^2 \delta_{S1}\right) + (-1)^S\left(\left\|a_{3\rm g}^S\right\|^2 - \left\|a_{3\rm u}^S\right\|^2\right)\right]\cos^2\theta_{12}$
	$+\frac{2}{3}\left(\left\|a_{2\rm g}^S\right\|^2 \delta_{S0} + \left\|a_{2\rm u}^S\right\|^2 \delta_{S1}\right)\sin^4\theta_{12} - \frac{2\sqrt{2}}{3}\,\mathrm{Re}\left(a_{2\rm g}^S a_{3\rm g}^{S*}\delta_{S0} + a_{2\rm u}^S a_{3\rm u}^{S*}\delta_{S1}\right)\sin^2\theta_{12}$
	$+\frac{4\sqrt{2}}{3}\,\mathrm{Re}\left(a_{1\rm g}^S a_{3\rm g}^{S*}\delta_{S0} + a_{1\rm u}^S a_{3\rm u}^{S*}\delta_{S1}\right)\cos\theta_{12}$
	$-\frac{2}{3}\,\mathrm{Re}\left(a_{1\rm g}^S a_{2\rm g}^{S*}\delta_{S0} + a_{1\rm u}^S a_{2\rm u}^{S*}\delta_{S1}\right)\cos\theta_{12}\sin^2\theta_{12}$
$^{1,3}\mathrm{F^o}$	$(1 + (-1)^S\cos\theta_{12})\left[\left\|a_{1\rm g}^S\right\|^2\left(\frac{2}{5} + \cos^2\theta_{12} - (-1)^S\cos\theta_{12}\right)\right.$
	$\left.+\frac{1}{15}\left\|a_{2\rm g}^S\right\|^2(4 + \cos^2\theta_{12} + (-1)^S\cos\theta_{12}) - 2\,\mathrm{Re}\left(a_{1\rm g}^S a_{2\rm g}^{S*}\right)(1 - (-1)^S 3\cos\theta_{12})\right]$
	$(1 - (-1)^S\cos\theta_{12})\left[-\left\|a_{1\rm u}^S\right\|^2\left(\frac{2}{5} + \cos^2\theta_{12} + (-1)^S\cos\theta_{12}\right)\right.$
	$\left.+\frac{1}{15}\left\|a_{2\rm u}^S\right\|^2(4 + \cos^2\theta_{12} - (-1)^S\cos\theta_{12}) - 2\,\mathrm{Re}\,\left(a_{1\rm u}^S a_{2\rm u}^{S*}\right)(1 + (-1)^S 3\cos\theta_{12})\right]$
$^{1,3}\mathrm{F^e}$	$\frac{1}{15}\sin^2\theta_{12}\left[4\left(\left\|a_{1\rm g}^S\right\|^2 + \left\|a_{1\rm u}^S\right\|^2\right) + \left(\left\|a_{2\rm g}^S\right\|^2 \delta_{S1} + \left\|a_{2\rm u}^S\right\|^2 \delta_{S0}\right)(5 + 3\cos^2\vartheta_{12})\right.$
	$\left.-(-1)^S\left(\left\|a_{1\rm g}^S\right\|^2 - \left\|a_{1\rm u}^S\right\|^2\right)(5\cos^2\vartheta_{12} - 1) + 16\,\mathrm{Re}\left(a_{1\rm g}^S a_{2\rm g}^{S*}\delta_{S1} + a_{1\rm u}^S a_{2\rm u}^{S*}\delta_{S0}\right)\cos\vartheta_{12}\right]$

2.2. Ne $1s^{-1}$ case

DA decay of the Ne $1s^{-1}\,{}^2\mathrm{S^e}$ vacancy state is possible to the three groups of final states in triply charged ions: $2s^{-2}2p^{-1}\,{}^2\mathrm{P^o}$, $2s^{-1}2p^{-2}\,{}^2\mathrm{S^e}$,${}^2\mathrm{D^e}$,${}^{2,4}\mathrm{P^e}$ and $2p^{-3}\,{}^2\mathrm{P^o}$, ${}^2\mathrm{D^o}$,${}^4\mathrm{S^o}$. The last state ${}^4\mathrm{S^o}$ cannot be populated by DA decay since the corresponding continuum state $\mathrm{S^o}$ does not exist: two electrons with $\ell_1 = \ell_2$ can only be in an *even* state. Since the initial state has $\mathrm{S^e}$ symmetry, according to the selection rules (9) the final continuum state of the two Auger electrons has the same symmetry and the same parity as the final ion. Therefore, there is no summation over L in expression (6), while the summation over S persists. For each transition the shape of the pattern is determined by one of the lines in table 1 and is similar to that presented in figure 1. If experimental resolution is not sufficient to resolve the final ionic terms, the angular distribution is an incoherent sum of the contributions from each ionic term with weights which should be determined from a model calculation.

2.3. Ar $2p^{-1}$ case

DA decay of the Ar $2p^{-1}\,{}^2P^o$ state is also possible to the three groups of final terms similar to those in Ne but for the configurations $3s^{-2}3p^{-1}$, $3s^{-1}3p^{-2}$ and $3p^{-3}$. Here, however, according to selection rules (9) for each final ionic term several $LS\pi$ continuum states contribute. For example, in the DA decay L_3–$M_1M_{23}M_{23}$ to the final ionic state ${}^2D^e$ the following continuum states contribute: ${}^{1,3}P^o$, ${}^{1,3}D^o$ and ${}^{1,3}F^o$ and the angular distribution is a weighted sum of expressions in the corresponding lines from table 1.

2.4. Angular patterns for the shake-off mechanism of double Auger decay

The energies of the emitted Auger electrons in DA decay are continuously distributed, and the probability of emission drastically depends on the energy sharing $\varepsilon_1/\varepsilon_2$. As in the case of DPI, the energy distribution in DA decay shows a strong sharp maximum in the domain $\varepsilon_1 \gg \varepsilon_2$ and a flat minimum at equal energy sharing $\varepsilon_1 = \varepsilon_2$. This behaviour of the energy distribution was predicted theoretically (Amusia *et al* 1992) and confirmed experimentally (Hindi *et al* 1996, Viefhaus *et al* 2002). It is naturally explained within the second order of the many-body perturbation theory (Amusia *et al* 1992) which includes all the main mechanisms of DA: 'knock-out' (the first Auger electron scatters and knocks out the second electron), 'shake-off' and the ground-state-correlation mechanism. Near the maximum ($\varepsilon_1 \gg \varepsilon_2$) the main contribution comes from the shake-off mechanism of DA decay, in which the fast electron is emitted in a normal Auger process and the slow electron is shaken off by a sudden change in the ionic potential. For the case of the Ne K–$L_1L_1L_{23}$ transition, Amusia *et al* (1992) calculated the angular distribution within the shake-off model at $\varepsilon_1 \gg \varepsilon_2$ and compared the results with more accurate MBPT calculations. Although the details of the two distributions are different, the qualitative behaviour is similar. Therefore, it is useful to consider the angular distributions in the DA process within the shake-off model.

In the simple version of the shake-off model, the slow electron undergoes monopole transition and therefore its orbital quantum number does not change in the decay. Furthermore, in the shake-off approximation the reduced matrix elements of DA decay may be presented as

$$\langle \alpha_f L_f, (\varepsilon_1\ell_1, \varepsilon_2\ell_2)L \| V^S \| \alpha_i L_i \rangle = \langle \alpha_f L_f, \varepsilon_1\ell_1 \| V^S \| \alpha_i L_i \rangle \langle \varepsilon_2\ell_2 | n_i\ell_i \rangle. \quad (19)$$

Here $\langle \varepsilon_2\ell_2 | n_i\ell_i \rangle$ is an overlap integral between single-electron continuum wavefunction of the shaken off electron and the wavefunction of this electron in the initial bound state. As argued above $\ell_2 = \ell_i$. The latter condition limits the summations in equation (8) to only a few terms and allows one to simplify the parametric forms of the probabilities F_{SL}. For example, it is easy to show that in the shake-off approximation the angular correlation function for the Ne $1s^{-1} \to 2s^{-2}2p^{-1}\,{}^2P^o$ transitions reduces to $A_1 + A_2 \cos\theta_{12}$, where A_1 and A_2 are constants. This function describes the dash-dotted curve in figure 6 (case 1) by Amusia *et al* (1992). The angular correlation for the transitions to the $2p^3\,{}^2P^o$ should have the form $A_1 + A_2 \cos^2\theta_{12}$, while for the $2p^3\,{}^2D^o$ final state it should be $A \sin^2\theta_{12}$.

3. Circular dichroism in the double Auger decay

Until now we have considered DA decay of an unpolarized initial vacancy state. However, for the vacancy angular momentum $\ell_i > 0$, sub-states with different projections of angular momentum may be non-statistically populated during the ionization process. Thus the ionic state may be polarized: aligned or oriented. We recall that the vacancy state is called aligned if the magnetic sub-states with opposite projections, $|l_i, m_i\rangle$ and $|l_i, -m_i\rangle$, are equally populated, while in a more general case of unequal population of such sub-states the vacancy state is called

oriented. The aligned p-vacancy is described by the alignment parameter $\mathcal{A}_{20}$; the oriented p-vacancy is described by the alignment parameter $\mathcal{A}_{20}$ and the orientation parameter $\mathcal{A}_{10}$. In particular, the vacancy produced by unpolarized or linearly polarized light is aligned; it is oriented if produced by circularly polarized light. It is known that the alignment produced by photoionization is generally very small (Berezhko *et al* 1978, Kleiman and Lohmann 2003). For example, for Ar 2p photoionization the alignment $\mathcal{A}_{20}$ is smaller than 0.07 for all photon energies from threshold up to 300 eV. In contrast, the orientation is rather large, $|\mathcal{A}_{10}| \sim 0.5$. Therefore, in the following we ignore the alignment and consider the effect of orientation on the angular distribution of the ejected electrons in DA decay. This effect is usually revealed in the circular dichroism study, i.e. measuring the difference between angular distributions excited by right and left circularly polarized light. The phenomenon of circular dichroism in two electron emission from atoms has been predicted theoretically for direct DPI (Berakdar and Klar 1992, 2001, Berakdar *et al* 1993), for two-step DPI (Schmidt 1994, Kabachnik and Schmidt 1995) and recently has been revealed experimentally for both processes (Soejima *et al* 1996, 1999, Viefhaus *et al* 1996, Mergel *et al* 1998). If DA decay is induced by photoionization with circularly polarized light, we can also expect the difference in angular distributions for right and left circularly polarized light, i.e. circular dichroism in DA process: a circular polarization of the photon results in an orientation of the produced vacancy state, which in turn influences the DA angular distributions. Note that in non-coincidence measurements the circular dichroism is zero: the angular distribution of emitted Auger electrons is not sensitive to circular polarization (see, e.g., Balashov *et al* (2000)).

To derive the circular dichroism, consider the probability of DA decay for the case of a non-equal population of the initial $|\alpha_i L_i M_{L_i}\rangle$ magnetic substates. We omit the spin variables in order to shorten the formulae and insert the spin index only in the final result. The initial state can be characterized by the density matrix $\langle \alpha_i L_i M_{L_i} | \rho^i | \alpha_i L_i M'_{L_i} \rangle$ or by a set of corresponding statistical tensors (state multipoles) $\rho_{kq}(L_i, L_i)$ (Blum 1996, Balashov *et al* 2000):

$$\langle \alpha_i L_i M_{L_i} | \rho^i | \alpha_i L_i M'_{L_i} \rangle = \sum_{kq} (-1)^{L_i - M'_{L_i}} \big(L_i M_{L_i}, L_i - M'_{L_i} | kq \big) \rho_{kq}(L_i, L_i). \tag{20}$$

The probability of two-electron emission may be written as a trace of the properly normalized final-state density matrix ρ^f

$$\begin{aligned} \frac{\mathrm{d}W}{\mathrm{d}\varepsilon_1 \, \mathrm{d}\mathbf{n_1} \, \mathrm{d}\mathbf{n_2}} &= \mathrm{Tr}\rho^f = \mathrm{Tr}(V \rho^i V^+) \\ &= 2\pi \sum_{M_{L_f} M_{L_i} M'_{L_i}} \mathcal{M}_{M_{L_i} M_{L_f}} \langle \alpha_i L_i M_{L_i} | \rho^i | \alpha_i L_i M'_{L_i} \rangle \mathcal{M}^*_{M'_{L_i} M_{L_f}}. \end{aligned} \tag{21}$$

Substituting here equations (2) and (20), performing necessary summations and accounting for the spin normalization factor, we obtain

$$\begin{aligned} \frac{\mathrm{d}W}{\mathrm{d}\varepsilon_1 \mathrm{d}\mathbf{n_1} \, \mathrm{d}\mathbf{n_2}} &= 2\pi \hat{S}_i^{-2} \sum_{kS} \sum_{LL'M_L} (-1)^{M_L + L_f + L_i + k} \hat{L} \hat{L}' (L M_L, L' - M_L | k0) \\ &\quad \times \begin{Bmatrix} L & L' & k \\ L_i & L_i & L_f \end{Bmatrix} \rho_{k0}(L_i, L_i) f_{SLM_L} f^*_{SL'M_L}, \end{aligned} \tag{22}$$

where we used the standard notations for the Wigner $6j$-symbol and directed the z-axis along the initial-state polarization (direction of the primary photon beam). For the non-polarized initial state only $k = 0$ contributes and expression (22) reduces to (6).

Equation (22) is written for the DA decay of an arbitrary polarized (along z-axis) initial state, characterized by the statistical tensors $\rho_{k0}(L_i, L_i)$. In photoionization by circularly

polarized light, however, in the dipole approximation the ionic state may only be oriented ($k = 1$) or aligned ($k = 2$). Since we ignore the alignment the only tensor which characterizes the anisotropy of the initial state is the orientation tensor $\rho_{10}(L_i, L_i)$ which is proportional to the P_3 Stokes parameter describing the circular polarization of the photon beam (Berezhko *et al* 1978). The change from right to left circular polarization means the change of signs of P_3 and $\rho_{10}(L_i, L_i)$. Circular dichroism in the angular distribution (CDAD) is defined as the difference between the angular distributions produced by right ($P_3 = +1$) and left ($P_3 = -1$) circularly polarized light, therefore

$$\begin{aligned}\mathrm{CDAD} &\equiv \left(\frac{\mathrm{d}W}{\mathrm{d}\varepsilon_1\,\mathrm{d}\mathbf{n_1}\,\mathrm{d}\mathbf{n_2}}\right)_+ - \left(\frac{\mathrm{d}W}{\mathrm{d}\varepsilon_1\,\mathrm{d}\mathbf{n_1}\,\mathrm{d}\mathbf{n_2}}\right)_- \\ &= 4\pi\hat{S}_i^{-2}\rho_{10}(L_i, L_i)\sum_S\sum_{LL'M_L}(-1)^{M_L+L_f+L_i+1}\hat{L}\hat{L}'(LM_L, L'-M_L|10) \\ &\quad\times\begin{Bmatrix} L & L' & 1 \\ L_i & L_i & L_f \end{Bmatrix} f_{SLM_L}f^*_{SL'M_L}, \end{aligned} \tag{23}$$

where $\rho_{10}(L_i, L_i)$ is taken for $P_3 = +1$.

Since the initial state with $L_i = 0$ cannot be oriented, the CDAD in this case vanishes. Therefore the CDAD for DA decay of Ne $1s^{-1}$ must be zero. Interestingly, equation (23) for the CDAD contains interference terms with different orbital angular momenta L of the electron pair, while different S and M_L contribute incoherently. Expression (23) may be used for calculations of the CDAD or for the qualitative analysis. Consider, for example, DA decay of the Ar $2p^{-1}$ vacancy to the $3p^{-2}3s^{-1}\,{}^2S^e$ state with emission of a pair of electrons in the state ${}^{1,3}P^o$. Here only $L = 1$ contributes, and the CDAD (23) reduces to

$$\mathrm{CDAD} = 2\pi\sqrt{2}\hat{S}_i^{-2}\rho_{10}(1, 1)\sum_S(|f_{S11}|^2 - |f_{S1-1}|^2). \tag{24}$$

Note that the state with $M_L = 0$ does not contribute due to the vanishing Clebsch–Gordan coefficient in (23). Substituting the expression (14) into (24) and using (16), we obtain

$$\mathrm{CDAD} = 2\pi\sqrt{2}\hat{S}_i^{-2}\rho_{10}(1, 1)\left(\sum_S(-1)^S\left|a_g^S\right\|a_u^S\right|\sin\Delta_{gu}^S\right)\sin\theta_1\sin\theta_2\sin(\phi_1 - \phi_2). \tag{25}$$

Here $\theta_{1,2}$ and $\phi_{1,2}$ are the polar and azimuthal angles of the electron emission and Δ_{gu}^S is a phase difference between a_g^S and a_u^S amplitudes. The CDAD depends not only on the mutual angle of the outgoing electrons θ_{12} (through the amplitudes $a_{g,u}^S$) but also on the individual angles of emission with respect to the photon beam direction. Expression (25) is very similar to the expression for the CDAD for He DPI (see, e.g., Briggs and Schmidt (2000)). The main difference is that for the DA decay both singlet and triplet states of the two-electron continuum contribute. Using (25) one can easily check that all kinematical properties of the CDAD in two-electron emission, derived for the DPI by Berakdar and Klar (1992), are the same for the DA decay: CDAD vanishes (i) when electrons are emitted in the plane containing the direction of the photon beam or (ii) when $\mathbf{n}_1 = \pm\mathbf{n}_2$ or (iii) when $\varepsilon_1 = \varepsilon_2$. (In the latter case $a_u^S = 0$ and consequently CDAD = 0.)

Similarly, expressions for the CDAD can be written for other transitions in Ar. However, due to interference of several L these expressions are too lengthy and complicated to be presented in this paper. All the kinematical properties of CDAD discussed above are also fulfilled for other transitions. A common feature of all expressions is also the fact that contributions of different total spins of the pair (S) are incoherent and only the imaginary part of the products of amplitudes, $\mathrm{Im}\left(a_g^S a_u^{S*}\right) = \left|a_g^S\right|\left|a_u^S\right|\sin\Delta_{gu}^S$, enters the final result. For

example, the CDAD should vanish for the transition Ar $2p^{-1} \rightarrow 3p^{-3}\,{}^4S^o$: the two Auger electrons are emitted in the state ${}^3P^e$ and, according to table 1, the amplitude a^S is either symmetric with respect to permutations (for $S = 1$) or antisymmetric (for $S = 0$). The product of the amplitudes is always zero.

Concluding this section we note that in order to observe the dichroism in the DA decay, the experiment should have sufficiently high resolution otherwise contributions of different final triply-ionized states may cancel each other. Besides, as it follows from general consideration (Berakdar and Klar 1992), the CDAD vanishes if one of the electrons is an s-electron. In the considered case of Ar $2p^{-1}$ decay, for example, a large contribution comes only from such pairs where one electron has $\ell = 0$. This is valid at least in the shake-off approximation (see discussion in the preceding section) and therefore is valid for highly asymmetric energy sharing ($\varepsilon_1 \gg \varepsilon_2$). This tendency also persists closer to equal energy sharing, thus diminishing the possible dichroism. According to our analysis of the shake-off approximation, the CDAD also vanishes at very high energy of one of the electrons. This is consistent with the dynamical behaviour of circular dichroism in DPI at very high energies (Berakdar 1998). The linear dichroism which was observed in He DPI (Soejima *et al* 1999) and which in the case of DA decay is connected with the alignment of the vacancy, can hardly be observed in experiment: the effect should be very small due to the small alignment.

4. Conclusions

We have analysed the general expression for the angular distributions of DA decay and suggested comparatively simple parametric forms of the angular correlation functions for various final electron states. The parametrization, however, is more complicated than for DPI since in all cases at least two sets of gerade and ungerade amplitudes describing singlet and triplet states of the two continuum electrons are necessary. We have found that within the conventional two-step description of the Auger process, when the decay of the ionic state is considered to be independent from its production stage, many properties of the DA emission are similar to the DPI case. All selection rules by Maulbetsch and Briggs (1995) derived from the symmetry properties of the two-electron wavefunction are fulfilled for DA decay. Also, the geometrical properties of the DPI angular distributions derived by Berakdar and Klar (1992) are appropriate for the DA process.

For an unpolarized initial state, different orbital angular momenta of the pair contribute incoherently to the angular correlation function in DA while for an oriented state their interference is important. In general, the angular correlation between two emitted electrons depends on the orientation of the initial state that may be observed as a circular dichroism in the photoinduced DA process. However, reliable calculations within an *ab initio* model are necessary in order to estimate the value of the effect.

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Appendix. Expressions for amplitudes

Below, we give partial wave expansions for the amplitudes $a_{\rm g}^S$ and $a_{\rm u}^S$ used in table 1 for various orbital angular momentum and parities of the emitted electron pair. We used the corresponding expressions from Manakov *et al* (1996) corrected according to Meremianin (1998). In the formulae of this appendix, indices j and n take values 1 and 2,

$^{2S+1}{\rm S}^{\rm e}$:

$$\begin{Bmatrix} a_{\rm g}^S \\ a_{\rm u}^S \end{Bmatrix} = \begin{Bmatrix} \delta_{S0} \\ \delta_{S1} \end{Bmatrix} \frac{1}{4\pi} \sum_\ell (-1)^\ell \hat{\ell} P_\ell(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell, \varepsilon_2 \ell)\, {\rm S}^{\rm e} \| V^S \| \alpha_i L_i \rangle. \tag{A.1}$$

$^{2S+1}{\rm P}^{\rm o}$:

$$a_{\rm g}^S = \frac{1}{\sqrt{2}}\left(b_1^S + (-1)^S b_2^S\right), \qquad a_{\rm u}^S = \frac{1}{\sqrt{2}}\left(b_1^S - (-1)^S b_2^S\right), \tag{A.2}$$

$$b_j^S = \frac{1}{4\pi} \sum_{\ell_1 \ell_2} \frac{1}{\sqrt{\ell_{\max}}} (-1)^{\ell_j + 1} P_{\ell_j}^{(1)}(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) {\rm P}^{\rm o} \| V^S \| \alpha_i L_i \rangle. \tag{A.3}$$

$^{2S+1}{\rm P}^{\rm e}$:

$$\begin{Bmatrix} a_{\rm g}^S \\ a_{\rm u}^S \end{Bmatrix} = \begin{Bmatrix} \delta_{S1} \\ \delta_{S0} \end{Bmatrix} \frac{\rm i}{4\pi} \sum_\ell (-1)^{\ell+1} \left[\frac{2\ell+1}{\ell(\ell+1)}\right]^{\frac{1}{2}} P_\ell^{(1)}(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell, \varepsilon_2 \ell) {\rm P}^{\rm e} \| V^S \| \alpha_i L_i \rangle. \tag{A.4}$$

$^{2S+1}{\rm D}^{\rm o}$:

$$a_{\rm g}^S = \frac{1}{\sqrt{2}}\left(b_1^S + (-1)^S b_2^S\right), \qquad a_{\rm u}^S = \frac{1}{\sqrt{2}}\left(b_1^S - (-1)^S b_2^S\right), \tag{A.5}$$

$$b_j^S = \frac{\rm i}{4\pi} \sum_{\ell_1 \ell_2} (-1)^{\ell_1} [\ell_1 \ell_2 (\ell_{\max}+1)]^{-\frac{1}{2}} P_{\ell_j}^{(2)}(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) {\rm D}^{\rm o} \| V^S \| \alpha_i L_i \rangle. \tag{A.6}$$

$^{2S+1}{\rm D}^{\rm e}$:

$$\begin{Bmatrix} a_{1{\rm g}}^S \\ a_{1{\rm u}}^S \end{Bmatrix} = \begin{Bmatrix} \delta_{S0} \\ \delta_{S1} \end{Bmatrix} \sum_{\ell_1 \ell_2} \left[C_1(\ell_1, \ell_2) \delta_{\ell_1 \ell_2} P_{\ell_1}^{(1)}(\cos\theta_{12}) - 2 C_2(\ell_1, \ell_2) P_{(\ell_1+\ell_2)/2}^{(2)}(\cos\theta_{12}) \right] \times \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2) {\rm D}^{\rm e} \| V^S \| \alpha_i L_i \rangle, \tag{A.7}$$

$$\begin{Bmatrix} a_{2{\rm g}}^S \\ a_{2{\rm u}}^S \end{Bmatrix} = \begin{Bmatrix} \delta_{S0} \\ \delta_{S1} \end{Bmatrix} \sum_\ell C_1(\ell, \ell) P_\ell^{(2)}(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell, \varepsilon_2 \ell) {\rm D}^{\rm e} \| V^S \| \alpha_i L_i \rangle, \tag{A.8}$$

$$a_{3{\rm g}}^S = \frac{1}{\sqrt{2}}\left(b_1^S + (-1)^S b_2^S\right), \qquad a_{3{\rm u}}^S = \frac{1}{\sqrt{2}}\left(b_1^S - (-1)^S b_2^S\right), \tag{A.9}$$

$$b_j^S = \sum_{\ell_1 \ell_2} C_2(\ell_1, \ell_2) \delta_{\ell_2 \ell_1 \pm 2} P_{\ell_j}^{(2)}(\cos\theta_{12}) \langle \alpha_f L_f, (\varepsilon_1 \ell_1, \varepsilon_2 \ell_2)\, {\rm D}^{\rm e} \| V^S \| \alpha_i L_i \rangle, \tag{A.10}$$

$$C_1(\ell, \ell) = \frac{(-1)^{\ell+1}}{4\pi} \left[\frac{6(2\ell+1)}{(2\ell-1)\ell(\ell+1)(2\ell+3)}\right]^{\frac{1}{2}}, \tag{A.11}$$

$$C_2(\ell_1, \ell_2) = \frac{(-1)^{\ell_1}}{4\pi} [\ell_{\max}(2\ell_{\max}-1)(\ell_{\max}-1)]^{-\frac{1}{2}}. \tag{A.12}$$

$^{2S+1}\mathrm{F}^{\mathrm{o}}$:

$$a^S_{ng} = \frac{1}{\sqrt{2}}\left(b^S_{1n} + (-1)^S b^S_{2n}\right), \qquad a^S_{nu} = \frac{1}{\sqrt{2}}\left(b^S_{1n} - (-1)^S b^S_{2n}\right), \tag{A.13}$$

$$b^S_{j1} = \sum_{\ell_1\ell_2} C(\ell_1,\ell_2)(-1)^j P^{(3)}_{\ell_j}(\cos\theta_{12})\langle \alpha_f L_f, (\varepsilon_1\ell_1,\varepsilon_2\ell_2)\mathrm{F}^{\mathrm{o}}\|V^S\|\alpha_i L_i\rangle, \tag{A.14}$$

$$b^S_{12} = -\sum_{\ell_1\ell_2} C(\ell_1,\ell_2)\left(3P^{(3)}_{\ell_2+1}(\cos\theta_{12}) - \frac{1}{2}(\ell_2-\ell_1+3)(\ell_1+\ell_2+4)P^{(2)}_{\ell_2}(\cos\theta_{12})\right) \times\langle \alpha_f L_f, (\varepsilon_1\ell_1,\varepsilon_2\ell_2)\,\mathrm{F}^{\mathrm{o}}|V^S|\alpha_i L_i\rangle, \tag{A.15}$$

$$b^S_{22} = \sum_{\ell_1\ell_2} C(\ell_1,\ell_2)\left(3P^{(3)}_{\ell_1+1}(\cos\theta_{12}) - \frac{1}{2}(\ell_1-\ell_2+3)(\ell_1+\ell_2+4)P^{(2)}_{\ell_1}(\cos\theta_{12})\right) \times\langle \alpha_f L_f, (\varepsilon_1\ell_1,\varepsilon_2\ell_2)\,\mathrm{F}^{\mathrm{o}}\|V^S\|\alpha_i L_i\rangle. \tag{A.16}$$

$^{2S+1}\mathrm{F}^{\mathrm{e}}$:

$$a^S_{ng} = \frac{1}{\sqrt{2}}\left(b^S_{1n} + (-1)^{S+1} b^S_{2n}\right), \qquad a^S_{nu} = \frac{1}{\sqrt{2}}\left(b^S_{1n} - (-1)^{S+1} b^S_{2n}\right), \tag{A.17}$$

$$b^S_{j1} = \mathrm{i}\sum_{\ell_1\ell_2} C(\ell_1,\ell_2)P^{(3)}_{\ell_j}(\cos\theta_{12})\langle \alpha_f L_f, (\varepsilon_1\ell_1,\varepsilon_2\ell_2)\,\mathrm{F}^{\mathrm{e}}\|V^S\|\alpha_i L_i\rangle, \tag{A.18}$$

$$b^S_{12} = \mathrm{i}\sum_{\ell_1\ell_2} C(\ell_1,\ell_2)\left(\frac{1}{4}(\ell_1-\ell_2+2)(\ell_1+\ell_2+3)P^{(2)}_{\ell_1}(\cos\theta_{12}) - P^{(3)}_{\ell_1+1}(\cos\theta_{12})\right) \times\langle \alpha_f L_f, (\varepsilon_1\ell_1,\varepsilon_2\ell_2)\,\mathrm{F}^{\mathrm{e}}\|V^S\|\alpha_i L_i\rangle, \tag{A.19}$$

$$b^S_{22} = \mathrm{i}\sum_{\ell_1\ell_2} C(\ell_1,\ell_2)\left(\frac{1}{4}(\ell_2-\ell_1+2)(\ell_1+\ell_2+3)P^{(2)}_{\ell_2}(\cos\theta_{12}) - P^{(3)}_{\ell_2+1}(\cos\theta_{12})\right) \times\langle \alpha_f L_f, (\varepsilon_1\ell_1,\varepsilon_2\ell_2)\,\mathrm{F}^{\mathrm{e}}\|V^S\|\alpha_i L_i\rangle, \tag{A.20}$$

$$C(\ell_1,\ell_2) = \frac{6(-1)^{\ell_2+1}}{\pi}\left[\frac{10(2\ell_1+1)(2\ell_2+1)(\ell_1+\ell_2-3)!}{(\ell_1-\ell_2+3)!(\ell_2-\ell_1+3)!(\ell_1+\ell_2+4)!}\right]^{\frac{1}{2}}. \tag{A.21}$$

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