Relativistic calculation of *CCV* and *CVV* Auger-electron spectra: Applications to $Ti_{0.5}Al_{0.5}N$ and Pd

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By keeping the interaction "classical," the nonrelativistic theory of *CCV* and *CVV* Auger-electron spectra (AES) is extended to a relativistic description, i.e., to a formulation in which the four participating states are described fully relativistically. It is shown that in the nonrelativistic limit the present approach yields exactly the previous nonrelativistic formulation. This is illustrated explicitly for the case of the Ti spectra of $Ti_{0.5}Al_{0.5}N$ for which nonrelativistic AES calculations were published recently. As a further example the $M_{4,5}VV$ AES is shown for pure metallic Pd and compared to existing experimental data as well as to a calculation using the intermediate-coupling scheme.

I. INTRODUCTION

Auger-electron spectroscopy (AES) is a relatively simple and efficient technique for analyzing chemical properties of solid matter. In the case of alloys the position of AES lines can help to identify the actual chemical composition, whereas the line shapes serve as indications for the nature of the local environment (chemical bonding). Concomitantly, being a many-electron process, it is an attractive tool for the study of electron-electron (hole-hole) correlations (for a comprehensive review on the AES processes the reader is referred to the book by Chattarji[1]).

The concept of theoretical valence-band spectroscopy is based on the interpretation of excitation spectra in terms of the ground-state electronic structure. This implies that the influence of electron correlation, which may be important particularly for Auger transitions, is neglected beyond the level of the local-density approximation (LDA). However, the straightforward inclusion of valence-band effects within this approach facilitates the understanding of the phenomena under consideration. The nonrelativistic formulation for valence-band *CCV* and *CVV* AES has been developed by Hörmandinger *et al.*[2,3] and was applied with success to early 3*d* transition-metal compounds. An apparent lack of this theory is that even for "light" elements the effect of spin-orbit splitting for the core states can be included merely by an *ad hoc* approximation, namely by weighting the nonrelativistic transition probabilities with the occupation for the core states. As will be shown in Sec. II E, this procedure turns out to be inconsistent for *CCV* AES, but it is consistent for *CVV* AES. In a relativistic formalism, however, even if relativistic effects in the valence band are negligible, the core states can be treated always properly leading to a more accurate description of the "cross sections." Quite clearly, for heavy elements, where relativistic effects are important also in the valence-band regime, the use of a relativistic theory is required in order to obtain a proper mapping of the valence band.

In Sec. II a relativistic theory for the *CCV* and *CVV* AES transition probabilities is derived, and their nonrelativistic limit is discussed. In Sec. III the results from a nonrelativistic and a relativistic formulation are compared for the $L_3M_{23}V$ and the L_3VV AES of Ti in $Ti_{0.5}Al_{0.5}N$. In Sec. IV a calculation for $M_{45}VV$ AES for pure Pd metal is presented. Since Pd metal exhibits a nearly filled 4*d* band, and subsequently the hole-hole repulsion should be considerably large, this case seems to provide an estimate about the range of applicability of the present method.

II. THEORY

A. General theory of the Auger process

The transition probability amplitude for two interacting electrons is given by Møller's relativistic formula,[1]

$$U_{12;34}=\int\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_1(\mathbf{r}_1)^+ \psi_2(\mathbf{r}_2)^+ W(\mathbf{r}_1,\mathbf{r}_2)\psi_3(\mathbf{r}_1)\psi_4(\mathbf{r}_2)\ , \tag{1}$$

where the initial and the final states for the two electrons are described by four-component Dirac wave functions $\psi_3(\mathbf{r}_1)$, $\psi_4(\mathbf{r}_2)$ and $\psi_1(\mathbf{r}_1)$, $\psi_2(\mathbf{r}_2)$, respectively, whereas $W(\mathbf{r}_1,\mathbf{r}_2)$ denotes the relativistic two-electron interaction operator.

The transition probability per unit time, as derived from time-dependent perturbation theory, includes both the direct ($D=U_{12;34}$) and the exchange ($E=U_{12,43}$) process and has to be summed over all the inobservables with respect to the given transition process (i.e., experimental technique),

$$\bar{P}=\frac{2\pi}{\hbar}[\overline{|D|^2}+\overline{|E|^2}-2\,\mathrm{Re}(\overline{D^*E})]\delta(\epsilon_1-\epsilon_3+\epsilon_2-\epsilon_4)\ . \tag{2}$$

In Eq. (2) the Dirac δ function represents the energy conservation and ϵ_i ($i=1,\ldots,4$) are the energy eigenvalues of the corresponding states.

B. The interaction operator

In a nonrelativistic (classical) treatment the relativistic two-electron interaction operator can be replaced by the

static Coulomb interaction,

$$W(\mathbf{r}_1,\mathbf{r}_2)=\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\ , \tag{3}$$

for which the Neumann expansion with respect to spherical coordinates can be used,

$$W(\mathbf{r}_1,\mathbf{r}_2)=e^2\sum_{\Lambda}\frac{4\pi}{(2\lambda+1)}\gamma_\lambda(r_1,r_2)Y_\Lambda(\Omega_1)^*Y_\Lambda(\Omega_2)\ . \tag{4}$$

Here $\Lambda=(\lambda,\nu)$ and $Y_\Lambda(\Omega)$ denote spherical harmonics. The angle-independent functions $\gamma_\lambda(r_1,r_2)$ are given by

$$\gamma_\lambda(r_1,r_2)=\frac{r_<^\lambda}{r_>^{\lambda+1}}\ , \tag{5}$$

where $r_<=\min\{r_1,r_2\}$ and $r_>=\max\{r_1,r_2\}$.

C. The participating states

1. Core states

The core wave functions are chosen to be atomiclike, i.e., they are eigenfunctions of J^2 and J_z,

$$\psi_Q(\epsilon;\mathbf{r})=\begin{bmatrix} g_\kappa(\epsilon;r)\chi_Q(\Omega) \\ if_\kappa(\epsilon;r)\chi_{\bar{Q}}(\Omega)\end{bmatrix}\ , \tag{6}$$

where $\chi_Q(\Omega)$ is a spin spherical harmonics, labeled by the relativistic quantum numbers, $Q=(\kappa,\mu)$ or $\bar{Q}=(-\kappa,\mu)$. In the following the quantum numbers j, l, $\bar{l}$, and S_κ are also used (see, e.g., Ref. 4). The radial functions, $g_\kappa(\epsilon;r)$ and $f_\kappa(\epsilon;r)$ are solutions of the coupled radial Dirac equations for a given core-energy eigenvalue ϵ.

2. Valence states

The sum of the tensorial product of the valence wave functions can be related to the one-particle Green's function in spin and configurational space as follows:

$$\sum_i \psi_i(\epsilon_i;\mathbf{r}_1)\psi_i(\epsilon_i;\mathbf{r}_2)^+\delta(\epsilon-\epsilon_i) =-\frac{1}{2\pi i}[G(\epsilon+i0;\mathbf{r}_1,\mathbf{r}_2)-G(\epsilon-i0;\mathbf{r}_1,\mathbf{r}_2)]\ , \tag{7}$$

whereby the side limits are indicated by $\epsilon\pm i0$. Using multiple-scattering theory, Eq. (7) can be written as[5] (in atomic Rydberg units: $e^2=2$, $\hbar=m=1$)

$$\sum_i \psi_i(\epsilon_i;\mathbf{r})\psi_i(\epsilon_i;\mathbf{r}')^+\delta(\epsilon-\epsilon_i) =-\frac{1}{\pi}\sum_{QQ'}Z_Q^m(\epsilon;\mathbf{r}_m)\,\mathrm{Im}[\tau_{QQ'}^{mn}(\epsilon)]Z_{Q'}^n(\epsilon;\mathbf{r}_n')^+\ , \tag{8}$$

where $\mathbf{r}_m$ and $\mathbf{r}_n'$ are the relative positions with respect to the mth and nth scattering centers, being located closest to $\mathbf{r}$ and $\mathbf{r}'$. The $Z_Q(\epsilon;\mathbf{r})$ functions are the corresponding regular scattering solutions,[6] and $\tau_{QQ'}^{mn}(\epsilon)$ denotes the scattering path operator.[7] Since AES is a site-specific spectroscopy, as an approximation, only site-diagonal ($m=n$) subblocks of the scattering path operator will be considered in Eq. (8). Furthermore, neglecting the off-diagonal matrix elements with respect to the angular-momentum indices, we can express the left-hand side of Eq. (8) in terms of the partial local densities of states (PDOS),[5]

$$n_\kappa(\epsilon)=-\frac{1}{\pi}R_\kappa(\epsilon)\sum_\mu \mathrm{Im}\tau_{QQ}(\epsilon)\ , \tag{9a}$$

$$R_\kappa(\epsilon)=\int_0^{R_s}r^2dr[G_\kappa(\epsilon;r)^2+F_\kappa(\epsilon;r)^2]\ . \tag{9b}$$

Consequently, Eq. (8) yields

$$\sum_i \psi_i(\epsilon_i;\mathbf{r})\psi_i(\epsilon_i;\mathbf{r}')^+\delta(\epsilon-\epsilon_i) =\sum_Q\frac{1}{(2j+1)}Z_Q(\epsilon;\mathbf{r})n_\kappa(\epsilon)Z_Q(\epsilon;\mathbf{r}')^+\ , \tag{10}$$

where for the sake of simplicity we omitted the site index. In Eq. (10) the scattering solutions $Z_Q(\epsilon;\mathbf{r})$ are normalized to unity within the muffin-tin radius R_s.

3. Continuum states

For a given positive energy the "free-space" plane waves corresponding to an eigenvalue $\mathbf{p}$ of the momentum operator span a two-dimensional subspace in the space of the four-component vectors, the basis set of which can be classified by spin-eigenvalues ($s=\pm\frac{1}{2}$),[8]

$$\Phi_s(\mathbf{p};\mathbf{r})=\left[\frac{W+mc^2}{2W}\right]^{1/2}\begin{bmatrix}\phi(s) \\ \dfrac{\sigma\cdot\mathbf{p}}{W+mc^2}\phi(s)\end{bmatrix}e^{i\mathbf{p}\cdot\mathbf{r}}\ , \tag{11}$$

where σ_i ($i=1,2,3$) are the Pauli matrices, $\phi(s)$ denotes a spin-eigenvector with the eigenvalue s, and $W=(m^2c^4+p^2c^2)^{1/2}$. In the weak relativistic limit the constant factor in Eq. (11) can be approximated by 1. The transformation from the plane-wave representation to the angular-momentum representation is given by[8]

$$\Phi_s(\mathbf{p};\mathbf{r})=4\pi\sum_Q i^l C(l\tfrac{1}{2}j;\mu-s,s)Y_{l,\mu-s}(\hat{\mathbf{p}})^*\psi_Q(p;\mathbf{r})\ , \tag{12a}$$

$$\psi_Q(p;\mathbf{r})=\begin{bmatrix} j_l(pr) & \chi_Q(\hat{\mathbf{r}}) \\ \dfrac{ipS_\kappa}{c}j_{\bar{l}}(pr) & \chi_{\bar{Q}}(\hat{\mathbf{r}})\end{bmatrix}\ , \tag{12b}$$

where the $C(l\frac{1}{2}j;\mu-s,s)$ denote Clebsch-Gordan coefficients. In the *single-site-approximation* a free-space solution described by Eqs. (12a) and (12b) is scattered by a single-scattering potential only,

$$\Psi_s(\mathbf{p};\mathbf{r})=4\pi\sum_Q i^l e^{i\delta_\kappa(\epsilon)}C(l\tfrac{1}{2}j;\mu-s,s)Y_{l,\mu-s}(\hat{\mathbf{p}})^*\tilde{Z}_Q(\epsilon;\mathbf{r})\ , \tag{13}$$

where $\epsilon=p^2/2m$, $\delta_\kappa(\epsilon)$ is the κ-like phase shift and $\tilde{Z}_Q(\epsilon;\mathbf{r})$ is a regular scattering solution with the following normalization at the muffin-tin radius:

$$\bar{Z}_Q(\epsilon;\mathbf{r})=\begin{bmatrix} [\cos\delta_\kappa(\epsilon)j_l(pr)-\sin\delta_\kappa(\epsilon)n_l(pr)]\chi_Q(\hat{\mathbf{r}}) \\ \frac{ipS_\kappa}{c}[\cos\delta_\kappa(\epsilon)j_{\bar{l}}(pr)-\sin\delta_\kappa(\epsilon)n_{\bar{l}}(pr)]\chi_{\bar{Q}}(\hat{\mathbf{r}}) \end{bmatrix} . \tag{14}$$

Equations (13) and (14) represent the relativistic analog of the *single-scatterer final state approximation.*[9,10]

Let us now denote a one-particle operator (both in configurational and spin space) by $\Pi(\mathbf{r},\mathbf{r}')$. Making use of the orthogonality relations for the spherical harmonics and the Clebsch-Gordan coefficients, the matrix element of this operator, with respect to the continuum states summed over the unobservables s and $\hat{\mathbf{p}}$, can be considerably reduced by the following identity:

$$\sum_{s=\pm 1/2}\int d\hat{\mathbf{p}}\int\int d\mathbf{r}\,d\mathbf{r}'\Psi_s(\mathbf{p};\mathbf{r})^+\Pi(\mathbf{r},\mathbf{r}')\Psi_s(\mathbf{p};\mathbf{r}')=(4\pi)^2\sum_Q\int\int d\mathbf{r}\,d\mathbf{r}'\bar{Z}_Q(\epsilon;\mathbf{r})^+\Pi(\mathbf{r},\mathbf{r}')\bar{Z}_Q(\epsilon;\mathbf{r}') , \tag{15}$$

which will be used in the next sections.

D. Core-core-valence Auger-electron spectra

According to Eqs. (1) and (2) and keeping in mind that we deal with a classical (scalar) interaction operator, the $\overline{|D|^2}$ contribution to $\bar{P}(\bar{P}_{D^2})$, for example, is given by

$$\begin{aligned}\bar{P}_{D^2}=\frac{2\pi}{\hbar}\sum_{\mu_1,\mu_3}\sum_{\text{states 4}}\sum_{\text{states 2}}\int d\epsilon\,\delta(\epsilon-\epsilon_4)\delta(\epsilon_1+\epsilon_2-\epsilon_3-\epsilon)\\ \times\int\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 W(\mathbf{r}_1,\mathbf{r}_2)W(\mathbf{r}_3,\mathbf{r}_4)\\ \times[\psi_1(\mathbf{r}_1)^+\psi_3(\mathbf{r}_1)][\psi_2(\mathbf{r}_2)^+\psi_4(\mathbf{r}_2)][\psi_3(\mathbf{r}_3)^+\psi_1(\mathbf{r}_3)][\psi_4(\mathbf{r}_4)^+\psi_2(\mathbf{r}_4)] ,\end{aligned} \tag{16}$$

where $[\psi_i(\mathbf{r})^+\psi_j(\mathbf{r})]$ denotes a scalar product of wave functions in spin space and the following identity is used:

$$\delta(\epsilon_1+\epsilon_2-\epsilon_3-\epsilon_4)=\int d\epsilon\,\delta(\epsilon-\epsilon_4)\delta(\epsilon_1+\epsilon_2-\epsilon_3-\epsilon) .$$

The degeneracy of the core states with respect to the quantum numbers of J_z is also taken into account.

From Eqs. (2), (10), and (16) one can immediately see that the contributions $\bar{P}_\alpha$ to the transition probability for the *CCV* AES can be set up in terms of PDOS's weighted by partial cross sections $\sigma_\kappa^\alpha(\epsilon)$,

$$\bar{P}_\alpha=\int d\epsilon\,\delta(\epsilon_1+\epsilon_2-\epsilon_3-\epsilon)\sum_\kappa n_\kappa(\epsilon)\sigma_\kappa^\alpha(\epsilon)\quad(\alpha=D^2,E^2,DE) . \tag{17}$$

Using Eqs. (6) and (15) for the partial cross sections related to the *direct term* one gets a rather complicated expression, namely,

$$\begin{aligned}\sigma_\kappa^{D^2}(\epsilon)=\frac{(4\pi)^4}{(2j+1)}\sum_{\mu_1,\mu_3,\mu}\sum_{Q_2,\Lambda,\Lambda'}\int\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4\frac{\gamma_\lambda(r_1,r_2)\gamma_{\lambda'}(r_3,r_4)}{(2\lambda+1)(2\lambda'+1)}Y_\Lambda(\Omega_1)^*Y_\Lambda(\Omega_2)Y_{\Lambda'}(\Omega_3)^*Y_{\Lambda'}(\Omega_4)\\ \times[g_{\kappa_1}(\epsilon_1;r_1)g_{\kappa_3}(\epsilon_3;r_1)\chi_{Q_1}(\Omega_1)^+\chi_{Q_3}(\Omega_1)\\ +f_{\kappa_1}(\epsilon_1;r_1)f_{\kappa_3}(\epsilon_3;r_1)\chi_{\bar{Q}_1}(\Omega_1)^+\chi_{\bar{Q}_3}(\Omega_1)]\\ \times[g_{\kappa_3}(\epsilon_3;r_3)g_{\kappa_1}(\epsilon_1;r_3)\chi_{Q_3}(\Omega_3)^+\chi_{Q_1}(\Omega_3)\\ +f_{\kappa_3}(\epsilon_3;r_3)f_{\kappa_1}(\epsilon_1;r_3)\chi_{\bar{Q}_3}(\Omega_3)^+\chi_{\bar{Q}_1}(\Omega_3)]\\ \times[\tilde{G}_{\kappa_2}(\epsilon_2;r_2)G_\kappa(\epsilon;r_2)\chi_{Q_2}(\Omega_2)^+\chi_Q(\Omega_2)\\ +\tilde{F}_{\kappa_2}(\epsilon_2;r_2)F_\kappa(\epsilon;r_2)\chi_{\bar{Q}_2}(\Omega_2)^+\chi_{\bar{Q}}(\Omega_2)]\\ \times[G_\kappa(\epsilon;r_4)\tilde{G}_{\kappa_2}(\epsilon_2;r_4)\chi_Q(\Omega_4)^+\chi_{Q_2}(\Omega_4)\\ +F_\kappa(\epsilon;r_4)\tilde{F}_{\kappa_2}(\epsilon_2;r_4)\chi_{\bar{Q}}(\Omega_4)^+\chi_{\bar{Q}_2}(\Omega_4)] ,\end{aligned} \tag{18}$$

where a universal constant factor of $2\pi e^4/\hbar$ has been omitted. Equation (18) clearly shows that the radial and angle-dependent parts are fairly well separated. The angular integrations can be carried out using Eq. (A1). Since the summation over the quantum numbers μ,μ_2 as well as over μ_1,μ_3 can be performed separately, the orthogonality relation for the Wigner $3j$ coefficients, Eq. (A3a) can be used. In accordance with Ref. 2 we introduce radial integrals,

$$I^{\lambda}[f_1 f_2|f_3 f_4]\equiv\int\int r_1^2 dr_1 r_2^2 dr_2\, f_1(r_1)f_2(r_1)\gamma_{\lambda}(r_1,r_2)f_3(r_2)f_4(r_2)\ . \tag{19}$$

Employing also Eq. (A2), the partial cross sections for the direct term can be written as

$$\sigma_{\kappa}^{D^2}(\epsilon)=(4\pi)^2\sum_{\kappa_2,\lambda}\frac{(2j_1+1)(2j_2+1)(2j_3+1)}{(2\lambda+1)}$$
$$\times(I^{\lambda}[g_{\kappa_1}g_{\kappa_3}|G_{\kappa}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda\kappa_3\rangle\langle\kappa\lambda\kappa_2\rangle+I^{\lambda}[g_{\kappa_1}g_{\kappa_3}|F_{\kappa}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda\kappa_3\rangle\langle-\kappa\lambda-\kappa_2\rangle$$
$$+I^{\lambda}[f_{\kappa_1}f_{\kappa_3}|G_{\kappa}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa_3\rangle\langle\kappa\lambda\kappa_2\rangle+I^{\lambda}[f_{\kappa_1}f_{\kappa_3}|F_{\kappa}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa_3\rangle\langle-\kappa\lambda-\kappa_2\rangle)^2\ . \tag{20}$$

In a similar way the partial cross sections corresponding to the *exchange term* in the transition probability are easily obtained by interchanging the initial states in the direct term

$$\sigma_{\kappa}^{E^2}(\epsilon)=(4\pi)^2\sum_{\kappa_2,\lambda}\frac{(2j_1+1)(2j_2+1)(2j_3+1)}{(2\lambda+1)}$$
$$\times(I^{\lambda}[g_{\kappa_1}G_{\kappa}|g_{\kappa_3}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda\kappa\rangle\langle\kappa_3\lambda\kappa_2\rangle+I^{\lambda}[g_{\kappa_1}G_{\kappa}|f_{\kappa_3}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda\kappa\rangle\langle-\kappa_3\lambda-\kappa_2\rangle$$
$$+I^{\lambda}[f_{\kappa_1}F_{\kappa}|g_{\kappa_3}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa\rangle\langle\kappa_3\lambda\kappa_2\rangle+I^{\lambda}[f_{\kappa_1}F_{\kappa}|f_{\kappa_3}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa\rangle\langle-\kappa_3\lambda-\kappa_2\rangle)^2\ . \tag{21}$$

When computing the partial cross sections of the *cross term*, the Wigner-Eckhart theorem can be used again for the angular integrations, but the sum over the quantum numbers of J_z can no longer be carried out separately. The contraction of four Wigner $3j$ symbols into one Wigner $6j$ symbol, Eq. (A4), however, formally simplifies the partial cross sections for the cross term to

$$\sigma_{\kappa}^{DE}(\epsilon)=(4\pi)^2\sum_{\kappa_2,\lambda,\lambda'}(-1)^{\lambda+\lambda'+1}(2j_1+1)(2j_2+1)(2j_3+1)\begin{Bmatrix}j_3 & \lambda' & j_2\\ j & \lambda & j_1\end{Bmatrix}$$
$$\times(I^{\lambda}[g_{\kappa_1}g_{\kappa_3}|G_{\kappa}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda\kappa_3\rangle\langle\kappa\lambda\kappa_2\rangle+I^{\lambda}[g_{\kappa_1}g_{\kappa_3}|F_{\kappa}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda\kappa_3\rangle\langle-\kappa\lambda-\kappa_2\rangle$$
$$+I^{\lambda}[f_{\kappa_1}f_{\kappa_3}|G_{\kappa}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa_3\rangle\langle\kappa\lambda\kappa_2\rangle+I^{\lambda}[f_{\kappa_1}f_{\kappa_3}|F_{\kappa}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa_3\rangle\langle-\kappa\lambda-\kappa_2\rangle)$$
$$\times(I^{\lambda'}[g_{\kappa_1}G_{\kappa}|g_{\kappa_3}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda'\kappa\rangle\langle\kappa_3\lambda'\kappa_2\rangle+I^{\lambda'}[g_{\kappa_1}G_{\kappa}|f_{\kappa_3}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda'\kappa\rangle\langle-\kappa_3\lambda'-\kappa_2\rangle$$
$$+I^{\lambda'}[f_{\kappa_1}F_{\kappa}|g_{\kappa_3}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda'-\kappa\rangle\langle\kappa_3\lambda'\kappa_2\rangle+I^{\lambda'}[f_{\kappa_1}F_{\kappa}|f_{\kappa_3}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda'-\kappa\rangle\langle-\kappa_3\lambda'-\kappa_2\rangle)\ . \tag{22}$$

E. The nonrelativistic limit

In this section it is shown that the expressions for the *CCV* AES obtained by a fully relativistic formalism are consistent in the nonrelativistic (NR) limit with the nonrelativistic derivation in Ref. 2.

In the nonrelativistic limit (i) the PDOS's are degenerate with respect to the total angular-momentum quantum number,

$$n_{\kappa}(\epsilon)=\frac{(2j+1)}{2(2l+1)}n_l(\epsilon)\ , \tag{23}$$

(ii) the small components of the radial wave functions vanish, while the large components become identical to the solutions of the corresponding radial Schrödinger equation, and (iii) since the core states are also degenerate with respect to j, an additional sum over these (degenerate) quantum numbers for both the initial and the final core states can be carried out.

Consequently, for the transition probability in the NR limit one can write

$$\bar{P}_{\alpha}^{\mathrm{NR}}=\int d\epsilon\,\delta(\epsilon_1+\epsilon_2-\epsilon_3-\epsilon)\sum_l n_l(\epsilon)\sigma_l^{\alpha}(\epsilon)\ , \tag{24a}$$

$$\sigma_l^{\alpha}(\epsilon)=\sum_{j_1,j_3}\sum_{j}\frac{(2j+1)}{2(2l+1)}\sigma_{\kappa}^{\alpha}(\epsilon)\ , \tag{24b}$$

where α can again be any of the symbols D^2, E^2, or DE. In the NR limit the cross sections for the direct term, Eq. (20), reduce therefore to

$$\sigma_l^{D^2}(\epsilon)=2(4\pi)^2\sum_{l_2,\lambda}\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{(2\lambda+1)}I^{\lambda}[R_{l_1}R_{l_3}|Z_l\tilde{Z}_{l_2}]^2\begin{bmatrix}l_1&\lambda&l_3\\0&0&0\end{bmatrix}^2\begin{bmatrix}l&\lambda&l_2\\0&0&0\end{bmatrix}^2$$
$$\times\tfrac{1}{4}\sum_{j_1,j_2,j_3,j}(2j+1)(2j_1+1)(2j_2+1)(2j_3+1)\begin{Bmatrix}l_1&\lambda&l_3\\j_3&\frac{1}{2}&j_1\end{Bmatrix}^2\begin{Bmatrix}l&\lambda&l_2\\j_2&\frac{1}{2}&j\end{Bmatrix}^2, \tag{25}$$

where the radial part for the core states is denoted by $R_l(\epsilon;r)$ and similarly, the radial part of the scattering solutions by $Z_l(\epsilon;r)$. Because of the orthogonality relation for the Wigner $6j$ symbols, Eq. (A3c), Eq. (25) is reduced to the expression given in Ref. 2, if multiplied by a factor of 2 to account correctly for the inobservable spin states. Nevertheless, it should be noted that if one wants to approximate the transition probability corresponding to an initial core state (l_3,j_3) and to a final core state (l_1,j_1) from a nonrelativistic calculation, the multiplication of the NR cross section by the occupational fractions

$$\frac{(2j_1+1)}{2(2l_1+1)}\frac{(2j_3+1)}{2(2l_3+1)}$$

does not work correctly, since after carrying out the sum over j,j_2 on the right-hand side (rhs) of Eq. (25), in each term a j_1,j_3 dependent factor of

$$(2j_1+1)(2j_3+1)\begin{Bmatrix}l_1&\lambda&l_3\\j_3&\frac{1}{2}&j_1\end{Bmatrix}^2$$

remains, which is still coupled to the summation variable λ.

The NR limit of the partial cross sections for the exchange term is given by

$$\sigma_l^{E^2}(\epsilon)=2(4\pi)^2\sum_{l_2,\lambda}\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{(2\lambda+1)}I^{\lambda}[R_{l_1}Z_l|R_{l_3}\tilde{Z}_{l_2}]^2\begin{bmatrix}l_1&\lambda&l\\0&0&0\end{bmatrix}^2\begin{bmatrix}l_3&\lambda&l_2\\0&0&0\end{bmatrix}^2$$
$$\times\tfrac{1}{4}\sum_{j_1,j_2,j_3,j}(2j+1)(2j_1+1)(2j_2+1)(2j_3+1)\begin{Bmatrix}l_1&\lambda&l\\j&\frac{1}{2}&j_1\end{Bmatrix}^2\begin{Bmatrix}l_3&\lambda&l_2\\j_2&\frac{1}{2}&j_3\end{Bmatrix}^2, \tag{26}$$

which upon using the orthogonality relation for the Wigner $6j$ coefficients, Eq. (A3c), also trivially reduces to the expression derived from the NR theory.

Including the extra factor 2 occurring in Eq. (2), the cross sections of the cross term in the NR limit are given by

$$\sigma_l^{DE}(\epsilon)=2(4\pi)^2\sum_{l_2,\lambda,\lambda'}(-1)^{\lambda+\lambda'}(2l_1+1)(2l_2+1)(2l_3+1)I^{\lambda}[R_{l_1}R_{l_3}|Z_l\tilde{Z}_{l_2}]I^{\lambda'}[R_{l_1}Z_l|R_{l_3}\tilde{Z}_{l_2}]$$
$$\times\begin{bmatrix}l_3&\lambda&l_1\\0&0&0\end{bmatrix}\begin{bmatrix}l_2&\lambda&l\\0&0&0\end{bmatrix}\begin{bmatrix}l&\lambda'&l_1\\0&0&0\end{bmatrix}\begin{bmatrix}l_2&\lambda'&l_3\\0&0&0\end{bmatrix}$$
$$\times-(\tfrac{1}{2})\sum_{j_1,j_2,j_3,j}(2j_1+1)(2j_2+1)(2j_3+1)(2j+1)$$
$$\times\begin{Bmatrix}j_3&\lambda'&j_2\\j&\lambda&j_1\end{Bmatrix}\begin{Bmatrix}l_3&\lambda&l_1\\j_1&\frac{1}{2}&j_3\end{Bmatrix}\begin{Bmatrix}l_2&\lambda&l\\j&\frac{1}{2}&j_2\end{Bmatrix}\begin{Bmatrix}l&\lambda'&l_1\\j_1&\frac{1}{2}&j\end{Bmatrix}\begin{Bmatrix}l_2&\lambda'&l_3\\j_3&\frac{1}{2}&j_2\end{Bmatrix}. \tag{27}$$

After eliminating the j-dependent contributions on the rhs of Eq. (27) in terms of Eq. (A5), one again obtains the result of the NR formulation.

F. Core-valence-valence Auger-electron spectra

Since in a *CVV* Auger transition both initial states (types 3 and 4) are valence states, one has to use the following identity for the Dirac δ function in Eq. (2):

$$\delta(\epsilon_1+\epsilon_2-\epsilon_3-\epsilon_4)=\int d\epsilon\,d\epsilon'\delta(\epsilon-\epsilon_3)\delta(\epsilon'-\epsilon_4)\delta(\epsilon_1+\epsilon_2-\epsilon-\epsilon')\ .$$

It is straightforward to show that the various contributions to the *CVV* AES transition probability can be set up in terms of a convolution of the partial local densities of states multiplied by partial cross sections,

$$\bar{P}_{\alpha}=\int d\epsilon\,d\epsilon'\delta(\epsilon_1+\epsilon_2-\epsilon-\epsilon')\sum_{\kappa,\kappa'}n_{\kappa}(\epsilon)n_{\kappa'}(\epsilon')\sigma_{\kappa\kappa'}^{\alpha}(\epsilon;\epsilon')\quad(\alpha=D^2,E^2,DE)\ . \tag{28}$$

The angular integrations and the subsequent summations over the quantum numbers of J_z can be performed analogous to Sec. II D leading to the following partial cross sections of the direct term, which is now identical to the exchange term

$$\sigma^{D^2}_{\kappa\kappa'}(\epsilon;\epsilon')=(4\pi)^2\sum_{\kappa_2,\lambda}\frac{(2j_1+1)(2j_2+1)}{(2\lambda+1)}(I^{\lambda}[g_{\kappa_1}G_{\kappa}|G_{\kappa'}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda\kappa\rangle\langle\kappa'\lambda\kappa_2\rangle+I^{\lambda}[g_{\kappa_1}G_{\kappa}|F_{\kappa'}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda\kappa\rangle\langle-\kappa'\lambda-\kappa_2\rangle$$
$$+I^{\lambda}[f_{\kappa_1}F_{\kappa}|G_{\kappa'}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa\rangle\langle\kappa'\lambda\kappa_2\rangle$$
$$+I^{\lambda}[f_{\kappa_1}F_{\kappa}|F_{\kappa'}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa\rangle\langle-\kappa'\lambda-\kappa_2\rangle)^2\ , \tag{29}$$

and of the cross term

$$\sigma^{DE}_{\kappa\kappa'}(\epsilon;\epsilon')=(4\pi)^2\sum_{\kappa_2,\lambda,\lambda'}(-1)^{\lambda+\lambda'+1}(2j_1+1)(2j_2+1)\begin{Bmatrix}j & \lambda' & j_2\\ j' & \lambda & j_1\end{Bmatrix}$$
$$\times(I^{\lambda}[g_{\kappa_1}G_{\kappa}|G_{\kappa'}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda\kappa\rangle\langle\kappa'\lambda\kappa_2\rangle+I^{\lambda}[g_{\kappa_1}G_{\kappa}|F_{\kappa'}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda\kappa\rangle\langle-\kappa'\lambda-\kappa_2\rangle$$
$$+I^{\lambda}[f_{\kappa_1}F_{\kappa}|G_{\kappa'}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa\rangle\langle\kappa'\lambda\kappa_2\rangle+I^{\lambda}[f_{\kappa_1}F_{\kappa}|F_{\kappa'}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda-\kappa\rangle\langle-\kappa'\lambda-\kappa_2\rangle)$$
$$\times(I^{\lambda'}[g_{\kappa_1}G_{\kappa'}|G_{\kappa}\tilde{G}_{\kappa_2}]\langle\kappa_1\lambda'\kappa'\rangle\langle\kappa\lambda'\kappa_2\rangle+I^{\lambda'}[g_{\kappa_1}G_{\kappa'}|F_{\kappa}\tilde{F}_{\kappa_2}]\langle\kappa_1\lambda'\kappa'\rangle\langle-\kappa\lambda'-\kappa_2\rangle$$
$$+I^{\lambda'}[f_{\kappa_1}F_{\kappa'}|G_{\kappa}\tilde{G}_{\kappa_2}]\langle-\kappa_1\lambda'-\kappa'\rangle\langle\kappa\lambda'\kappa_2\rangle$$
$$+I^{\lambda'}[f_{\kappa_1}F_{\kappa'}|F_{\kappa}\tilde{F}_{\kappa_2}]\langle-\kappa_1\lambda'-\kappa'\rangle\langle-\kappa\lambda'-\kappa_2\rangle)\ . \tag{30}$$

Using the procedure of Sec. II E it is easy to show that the NR limit for the CVV AES transition probabilities is also consistent with the previous NR formulation.[3,11] It is worthwhile to mention that in this case the splitting of the NR transition probabilities corresponding to the final core states (l_1,j_1) is correct for both the direct and cross terms when the occupational fraction, $(2j_1+1)/[2(2l_1+1)]$ is taken into account.

G. Restrictions of the theory

The relativistic theory of AES presented in the previous sections is based on a time-dependent perturbation theory for an operator deduced from the quantum electrodynamics and on transition probabilities as evaluated by using the fully relativistic description for the participating electron states. In order to account for core-hole lifetime effects the spectra are convoluted by a Lorentzian of constant half width. For valence-band lifetime effects we use a Lorentzian with energy-dependent half width decreasing quadratically from the band bottom to zero at the Fermi energy. The spectrometer resolution is simulated by a convolution with a Gaussian of constant half width.

The main restrictions of the present theory are as follows.

(i) Since it is a one-particle theory, only noninteracting excited hole states can be considered. According to the Cini-Sawatzky theory,[12,13] for solids with completely filled bands the two-hole propagator is renormalized via the repulsion energy between the two holes (U). This theory has been extended to systems with open bands and to include spin-orbit interaction (see Ref. 14 and also references therein). However, only constant (energy independent) cross sections enter this theory.

(ii) In some cases the hole on a lower core subshell will be filled from the higher subshell by a rapid Coster-Kronig transition, which has to be viewed as a competing process to AES. This can considerably reduce the theoretical AES intensity arising from the lower subshell.

(iii) Because of the usual short mean free path of the "free" electrons in solids, the escape depth for the Auger electrons is typically about 10 Å, which corresponds to no more than 4–5 atomic layers at the surface. Therefore, surface effects can play an important role in AES. However, with some modifications, such as a proper summation over layers, the present theory can also be used for semi-infinite systems.

III. AES FOR Ti IN $Ti_{0.5}Al_{0.5}N$

In a recent paper[15] we presented nonrelativistic calculations for the $L_3M_{23}V$ and the L_3VV AES of Ti in $Ti_{0.5}Al_{0.5}N$. Since the relativistic effects in the valence band are fairly negligible for this system, it seems to be a suitable system to confirm the relativistic formulation described in the previous section. For the relativistic calculations, according to Eq. (23), the κ-like PDOS's were approximated by their NR counterparts. In analogy to the previous calculation, a half width of 0.5 eV at the band bottom for lifetime broadening was used. The spectrometer resolution function was taken to be the same as in Ref. 15.

The results for the $L_3M_{23}V$ AES are shown in Fig. 1. In the NR calculation, the ratio of the magnitudes for the L_3M_2V and L_3M_3V component spectra is 1:2. This ratio is reduced to about 1:5 in the relativistic calculation, which, as stressed in Sec. II E, clearly illustrates a possible inadequacy of the NR formulation. Nevertheless, since the spin-orbit splitting for the M_2 and M_3 core lev-

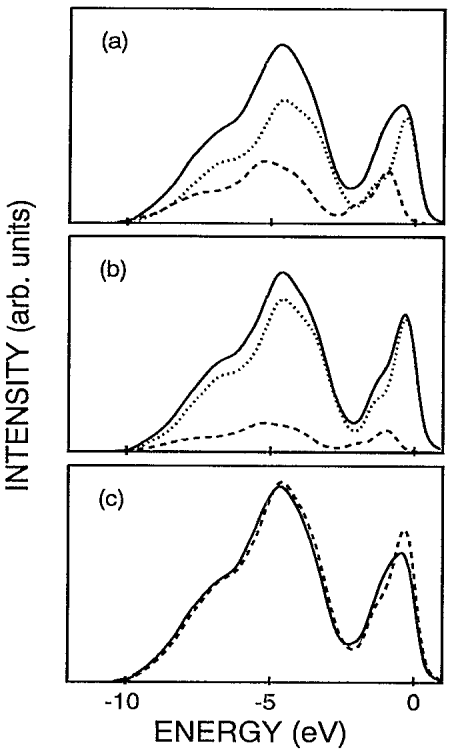

FIG. 1. Calculated $L_3M_{23}V$ AES for Ti in $Ti_{0.5}Al_{0.5}N$. (a) shows the results from a nonrelativistic formalism (Ref. 15), while (b) displays those using the present relativistic theory. In both panels the dashed line corresponds to the L_3M_2V, the dotted line to the L_3M_3V contribution, and the solid line to the total spectrum. The total spectra are compared to each other in (c) (solid line, nonrelativistic; dotted line, relativistic). The zero of the energy scale refers to the highest possible kinetic energy for the outgoing electrons.

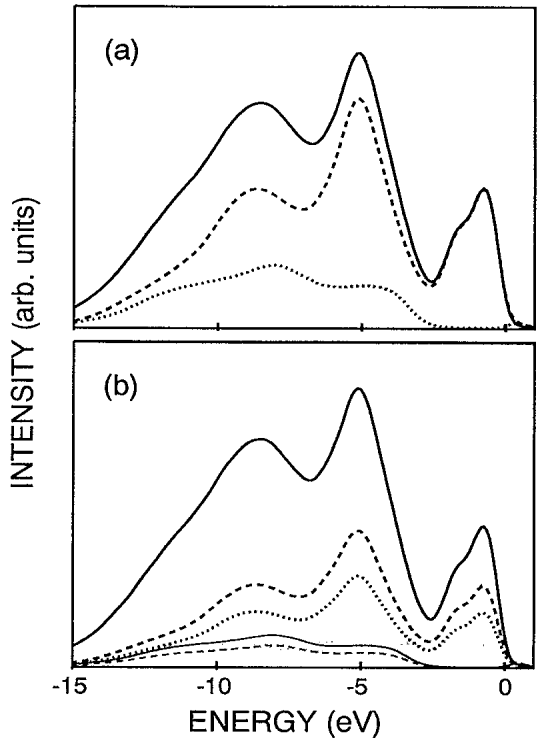

FIG. 2. L_3VV AES for Ti in $Ti_{0.5}Al_{0.5}N$, as calculated nonrelativistically (a) (Ref. 15) and relativistically (b) (present work). The total spectra are shown by solid lines. In (a) the dashed line refers to the (d,d) part of the spectrum, and the dotted line to the (p,d) part of the spectrum. In (b) the following (κ,κ')-like contributions are shown: $(2,-3)$, dashed line; $(-3,-3)$, dotted line; $(-2,-3)$, thin solid line; and $(-2,2)$, thin dashed line. The zero of the energy scale refers to the highest possible excitation energy for the Auger electrons.

els is fairly small (~ 0.6 eV), the main broad peak around 5 eV in the total spectrum remains in fact unmodified in both types of calculation. The difference between the nonrelativistic and relativistic calculation for the component spectra to be superposed shows up in a narrowing of the peak near the top of the spectrum.

The results for the L_3VV Auger-electron spectra calculated in the nonrelativistic and relativistic approaches are nearly identical. It is interesting, however, to investigate the partial, i.e., the (l,l')-like as well as the (κ,κ')-like components of these spectra (see also Ref. 3). As can be seen from Fig. 2(a) in the NR case the spectrum has predominantly (d,d)-like and also some (p,d)-like character. Within the relativistic formalism each of these two components will further be split up into (κ,κ')-like components, namely, into the $(-3,-3),(2,-3),(2,2)$ and into the $(1,-3),(1,2),(-2,-3),(-2,2)$ partial spectra, respectively. As indicated by Fig. 2(b), the (2,2) contribution is suppressed in the first case, while in the second case the $(1,-3)$ and the (1,2) partial contributions are suppressed. This again shows that even for this nearly nonrelativistic case the (κ,κ')-like partial components to the intensity are not simply proportional via corresponding degeneracies to the (l,l')-like partial spectra.

IV. $M_{45}VV$ AES FOR PD

As a further application of the present theory the Pd $M_{45}VV$ AES is calculated because of the possibility to compare our calculation with the experimental data[16] and also with a calculation using the Cini-Sawatzky theory in the intermediate-coupling scheme as extended to open bands and including spin-orbit effects.[14] This second comparison is of particular interest, because both theories incorporate relativistic effects and use results from relativistic band-structure calculations.

In our calculations we used the potential and PDOS's from a self-consistent-field fully relativistic Korringa-Kohn-Rostocker (SCF-RKKR) calculation.[17] The half width of the Lorentzian for the valence-band lifetime broadening was taken to be 0.5 eV at the band bottom. As a suitable half width for the spectrometer broadening function 1 eV was used, since for values less than 1 eV the fine details of the valence density of states showed up in the calculated spectrum, which are apparently absent in the experimental data. The splitting of the M_4 and M_5 core states of about 5.63 eV is also consistent to the value used in Ref. 14.

Figure 3 shows the result of our calculation together with the experimental data and the result of Ref. 14.

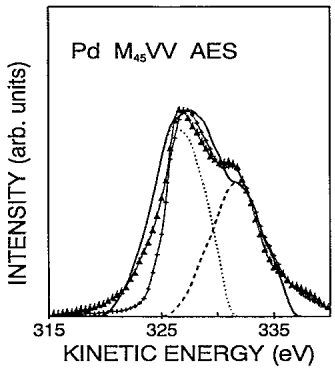

FIG. 3. $M_{45}VV$ spectra for pure Pd metal. The triangles refer to the experiment (Ref. 16), the crosses to the result of the intermediate-coupling theory (Ref. 14), and the thick solid line to the present approach. For the latter case the M_4VV (dashed line) and M_5VV (dotted line) components are also presented. Thin solid lines serve as a guide for eye.

From the latter two we subtracted the background intensity as given in Ref. 14. Our calculated total spectrum was normalized to the maximum of the main peak in the experimental curve. Also included in Fig. 3 are the M_4VV and M_5VV contributions to the present theoretical spectrum. Since, as mentioned already in Sec. II G, our theory does not include corrections due to a possible Coster-Kronig transition, we did not modify the intensity ratio for these two contributions, which was essentially a fitting parameter for the calculation by Cini and Verdozzi.[14]

Considering our calculation, the half width of the spectrum and the relative position between the large peak and the shoulder agree within less than 1 eV with the experiment. Beyond the fact that our calculated spectrum depicts the overall shape of the measured spectrum quite well, there are some features less well reproduced, namely the width of the main peak is overestimated and therefore the shoulder is less pronounced. Unfortunately, the authors of Ref. 14 did not present their component spectra, thus a detailed discussion concerning the two theoretical results is hardly possible.

V. CONCLUSIONS

In this paper we developed a fully relativistic treatment for valence-band Auger-electron spectra. We would like to stress that, aside from broadening parameters for lifetime effects and finite spectrometer resolution, our theory is essentially *parameter free*, whereas the model mentioned above uses parameters which are extracted in part from other calculations or measurements or are adjusted to fit the experimental spectrum (see also a similar type of calculation in Ref. 18). Our theory can be applied immediately to a large variety of systems, once a realistic electronic structure calculation is provided. We believe that the present approach is especially suitable for all cases where (i) cross sections are important as, for example, in a comparison of relative intensities for different types of spectra, and (ii) concentration-dependent changes for both the cross sections and PDOS's are important, i.e., when considering alloys and nonstoichiometric systems.

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APPENDIX

The angle integration required in the evaluation of the AES partial cross sections can be carried out in terms of the Wigner-Eckhart theorem as follows:

$$\int d\Omega \chi_Q(\Omega)^+ Y_\Lambda(\Omega)\chi_{Q'}(\Omega) = (-1)^{j+j'+\lambda-\mu+1/2}\left[\frac{(2j+1)(2j'+1)(2\lambda+1)}{4\pi}\right]^{1/2} \times \langle \kappa\lambda\kappa'\rangle \begin{pmatrix} j & \lambda & j' \\ -\mu & \nu & \mu' \end{pmatrix}, \tag{A1}$$

where

$$\langle \kappa\lambda\kappa'\rangle \equiv [(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} l & \lambda & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l & \lambda & l' \\ j' & \frac{1}{2} & j \end{Bmatrix}, \tag{A2}$$

and the symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \text{ and } \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix}$$

denote Wigner $3j$ and $6j$ coefficients, respectively, for which the following orthogonality relations hold[19]:

$$\sum_{m_1,m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{\delta_{j_3 j_3'}\delta_{m_3 m_3'}}{2j_3+1}, \tag{A3a}$$

$$\sum_{j_3,m_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1 m_1'}\delta_{m_2 m_2'}, \tag{A3b}$$

$$\sum_j (2j+1) \begin{Bmatrix} j_1 & j_2 & j' \\ j_3 & j_4 & j \end{Bmatrix} \begin{Bmatrix} j_1 & j_2 & j'' \\ j_3 & j_4 & j \end{Bmatrix} = \frac{\delta_{j'j''}}{2j'+1}, \tag{A3c}$$

with δ being the Kronecker symbol. The following relation between the $3j$ and the $6j$ symbols should also be noted[19]:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix} = \sum_{\substack{M_1,M_2,M_3 \\ m_1,m_2,m_3}} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3} \times \begin{bmatrix} J_1 & J_2 & j_3 \\ M_1 & -M_2 & m_3 \end{bmatrix} \begin{bmatrix} J_2 & J_3 & j_1 \\ M_2 & -M_3 & m_1 \end{bmatrix} \begin{bmatrix} J_3 & J_1 & j_2 \\ M_3 & -M_1 & m_2 \end{bmatrix} \begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{bmatrix} . \quad \text{(A4)}$$

Finally, a combined application of Eqs. (A3a), (A3b), (A3c), and (A4) leads to the identity

$$\begin{Bmatrix} l_3 & \lambda' & l_2 \\ l & \lambda & l_1 \end{Bmatrix} = -\tfrac{1}{2} \sum_{j_1,j_2,j_3,j} (2j_1+1)(2j_2+1)(2j_3+1)(2j+1) \times \begin{Bmatrix} j_3 & \lambda' & j_2 \\ j & \lambda & j_1 \end{Bmatrix} \begin{Bmatrix} l_3 & \lambda & l_1 \\ j_1 & \tfrac{1}{2} & j_3 \end{Bmatrix} \begin{Bmatrix} l_2 & \lambda & l \\ j & \tfrac{1}{2} & j_2 \end{Bmatrix} \begin{Bmatrix} l & \lambda' & l_1 \\ j_1 & \tfrac{1}{2} & j \end{Bmatrix} \begin{Bmatrix} l_2 & \lambda' & l_3 \\ j_3 & \tfrac{1}{2} & j_2 \end{Bmatrix} . \quad \text{(A5)}$$

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