Appendix D
Applications of Angular Momentum Algebra

In this appendix we consider four applications of the angular momentum algebra theory described in Appendices A and B. In these applications we obtain explicit expressions for quantities that occur in the main body of this monograph. We first derive expressions for the long-range multipole potential coefficients, which arise in our discussion of both non-relativistic and relativistic electron–atom and electron–ion collisions. We then derive expressions for the long-range multipole potentials which arise in R-matrix–Floquet theory and in time-dependent R-matrix theory of multiphoton processes. Finally, we obtain an expression for the atomic differential photoionization cross section.

In these applications it is important to adopt a consistent phase convention throughout the analysis, although the final physical observables will not depend on the phase convention chosen. We have pointed out in Appendix B.4 that two phase conventions for spherical harmonics have been used in applications, referred to as the Condon–Shortley and the Fano–Racah phase conventions. In this appendix we adopt the Fano–Racah phase convention which has been used in many applications of R-matrix theory. However, in order to illustrate the importance of adopting a consistent phase convention in the analysis, we also derive explicit expressions in Appendix D.1.1 for the long-range multipole potential coefficients in non-relativistic electron collisions with atoms and ions when the Condon–Shortley phase convention is adopted.

D.1 Long-Range Electron–Atom Potential Coefficients

D.1.1 Non-relativistic Collisions

In this section we derive explicit expressions for the long-range multipole potential coefficients in non-relativistic electron collisions with atoms and ions using both the Fano–Racah and the Condon–Shortley phase conventions. We consider first the expression obtained using the Fano–Racah phase convention.

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We have shown in Sect. 5.1.3 that the long-range local potential completely describes the electron–target interaction beyond some radius a_0 where the non-local exchange and correlation potentials are negligible. This enables R-matrix propagator methods to be used to solve the resultant coupled differential equations (5.29) in this external region. We also note that the long-range potential coefficients are used in the development of asymptotic expansion methods for solving these equations, described in Appendix F.1.

In the absence of relativistic effects, the long-range potential coefficients $\alpha^{\Gamma}_{ii'\lambda}$ in (2.73) and (5.30) are defined by the equation

$$\alpha^{\Gamma}_{ii'\lambda} = \langle r^{-1}_{N+1} \overline{\Phi}^{\Gamma}_{i}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) \left| \sum_{k=1}^{N} r^{\lambda}_{k} P_{\lambda}(\cos\theta_{kN+1}) \right| \times r^{-1}_{N+1} \overline{\Phi}^{\Gamma}_{i'}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle', \tag{D.1}$$

where the integration in this equation is carried out over all the $(N+1)$-electron space and spin coordinates except the radial coordinate of the $(N+1)$th or scattered electron. We expand $P_{\lambda}(\cos\theta_{kN+1})$ in (D.1) in terms of spherical harmonics satisfying the Fano–Racah phase convention, using (B.77) which we rewrite here as

$$P_{\lambda}(\cos\theta_{kN+1}) = \frac{4\pi}{2\lambda+1} \sum_{m=-\lambda}^{+\lambda} \mathcal{Y}_{\lambda m}(\theta_k, \phi_k) \mathcal{Y}^{*}_{\lambda m}(\theta_{N+1}, \phi_{N+1}), \tag{D.2}$$

and we define the channel functions $\overline{\Phi}^{\Gamma}_{i}$ in (D.1) as follows

$$\overline{\Phi}^{\Gamma}_{i}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) = \sum_{M_{L_i} m_{\ell_i}} \sum_{M_{S_i} m_i} (L_i M_{L_i} \ell_i m_{\ell_i} | L M_L) \times (S_i M_{S_i} \tfrac{1}{2} m_i | S M_S) \Phi^{\mathrm{FR}}_{i}(\mathbf{X}_N) \times \mathcal{Y}_{\ell_i m_{\ell_i}}(\theta_{N+1}, \phi_{N+1}) \chi_{\frac{1}{2} m_i}(\sigma_{N+1}) \tag{D.3}$$

and an analogous expression for $\overline{\Phi}^{\Gamma}_{i'}$. We also introduce the tensor operators

$$M^{\mathrm{FR}}_{\lambda m} = \left(\frac{4\pi}{2\lambda+1}\right)^{1/2} \sum_{k=1}^{N} r^{\lambda}_{k} \mathcal{Y}_{\lambda m}(\theta_k, \phi_k) \tag{D.4}$$

and

$$C^{\mathrm{FR}}_{\lambda m} = \left(\frac{4\pi}{2\lambda+1}\right)^{1/2} \mathcal{Y}_{\lambda m}(\theta_{N+1}, \phi_{N+1}). \tag{D.5}$$

Substituting these results into (D.1) and carrying out the summations over the spin magnetic quantum numbers, which yield $\delta_{S_i S_{i'}}$, then gives

$$\left(\alpha_{ii'\lambda}^{\Gamma}\right)^{\mathrm{FR}} = \sum_{m} \sum_{M_{L_i} m_{\ell_i}} \sum_{M_{L_{i'}} m_{\ell_{i'}}} \langle \Phi_i^{\mathrm{FR}}(\mathbf{X}_N)|M_{\lambda m}^{\mathrm{FR}}|\Phi_{i'}^{\mathrm{FR}}(\mathbf{X}_N)\rangle$$
$$\times \langle \mathcal{Y}_{\ell_i m_{\ell_i}}(\theta_{N+1},\phi_{N+1})|C_{\lambda m}^{\mathrm{FR}*}|\mathcal{Y}_{\ell_{i'} m_{\ell_{i'}}}(\theta_{N+1},\phi_{N+1})\rangle$$
$$\times (L_i M_{L_i} \ell_i m_{\ell_i}|L M_L)(L_{i'} M_{L_{i'}} \ell_{i'} m_{\ell_{i'}}|L M_L)\delta_{S_i S_{i'}}. \qquad (D.6)$$

The integration over the scattered electron angular coordinates $\hat{\mathbf{r}}_{N+1}$ in (D.6) can be carried out using (B.71) yielding

$$\langle \mathcal{Y}_{\ell_i m_{\ell_i}}(\theta_{N+1},\phi_{N+1})|C_{\lambda m}^{\mathrm{FR}*}|\mathcal{Y}_{\ell_{i'} m_{\ell_{i'}}}(\theta_{N+1},\phi_{N+1})\rangle$$
$$= \mathrm{i}^{\ell_{i'}-\ell_i-\lambda}(-1)^m \left[\frac{2\ell_{i'}+1}{2\ell_i+1}\right]^{1/2} (\lambda\, -m \ell_{i'} m_{\ell_{i'}}|\ell_i m_{\ell_i})(\lambda 0 \ell_{i'} 0|\ell_i 0). \qquad (D.7)$$

In order to carry out the summation over the orbital magnetic quantum numbers, we introduce the reduced multipole moments of the target expressed as $\langle \alpha_i L_i S_i \pi_i||M_\lambda^{\mathrm{FR}}||\alpha_{i'} L_{i'} S_{i'} \pi_{i'}\rangle$ which are defined by the equation

$$\langle \Phi_i^{\mathrm{FR}}(\mathbf{X}_N)|M_{\lambda m}^{\mathrm{FR}}|\Phi_{i'}^{\mathrm{FR}}(\mathbf{X}_N)\rangle = (2L_i+1)^{-1/2}(L_{i'} M_{L_{i'}} \lambda m|L_i M_{L_i})$$
$$\times \langle \alpha_i L_i S_i \pi_i||M_\lambda^{\mathrm{FR}}||\alpha_{i'} L_{i'} S_{i'} \pi_{i'}\rangle. \qquad (D.8)$$

This result follows from the Wigner–Eckart theorem (Wigner [965], Eckart [282]) which states that the dependence of the matrix element $\langle \Phi_i|M_{\lambda m}|\Phi_{i'}\rangle$ on the magnetic quantum numbers M_{L_i}, $M_{L_{i'}}$ and m is entirely contained in the Clebsch–Gordan coefficient $(L_{i'} M_{L_{i'}} \lambda m|L_i M_{L_i})$. The reduced multipole moments of the target thus depend on the detailed atomic structure of the target states but not on their magnetic quantum numbers.

We now collect together the terms involving the orbital magnetic quantum numbers from (D.6), (D.7) and (D.8). We define the summation

$$S = \sum_{m} \sum_{M_{L_i} m_{\ell_i}} \sum_{M_{L_{i'}} m_{\ell_{i'}}} (-1)^m (L_i M_{L_i} \ell_i m_{\ell_i}|L M_L)(L_{i'} M_{L_{i'}} \ell_{i'} m_{\ell_{i'}}|L M_L)$$
$$\times (\lambda\, -m \ell_{i'} m_{\ell_{i'}}|\ell_i m_{\ell_i})(L_{i'} M_{L_{i'}} \lambda m|L_i M_{L_i}). \qquad (D.9)$$

This summation can be evaluated using the symmetry property of the Clebsch–Gordan coefficient

$$(\lambda\, -m \ell_{i'} m_{\ell_{i'}}|\ell_i m_{\ell_i}) = (-1)^{\ell_i-\ell_{i'}+m} \left[\frac{2\ell_i+1}{2\ell_{i'}+1}\right]^{1/2} (\lambda m \ell_i m_{\ell_i}|\ell_{i'} m_{\ell_{i'}}), \qquad (D.10)$$

which follows from (A.21) and (A.23) and the definition of the Racah coefficient given by (A.46). We then obtain

$$S = (-1)^{\ell_i-\lambda-L+L_i}\,[(2\ell_i+1)(2L_i+1)]^{1/2}\,W(L_iL_{i'}\ell_i\ell_{i'};\lambda L), \tag{D.11}$$

where we have also used the symmetry properties of the Racah coefficients given by (A.48) and (A.49). Using this result, we find that the expression given by (D.6) for the long-range potential coefficients reduces to

$$\begin{aligned}\left(\alpha^{\Gamma}_{ii'\lambda}\right)^{\mathrm{FR}} &= \mathrm{i}^{\ell_i+\ell_{i'}-\lambda}(-1)^{L_i-L}(2\ell_i+1)^{1/2}(\ell_i0\lambda0|\ell_{i'}0)W(L_iL_{i'}\ell_i\ell_{i'};\lambda L)\\ &\times\langle\alpha_iL_iS_i\pi_i||M^{\mathrm{FR}}_{\lambda}||\alpha_{i'}L_{i'}S_{i'}\pi_{i'}\rangle\delta_{S_iS_{i'}},\end{aligned} \tag{D.12}$$

where we note that the term $\mathrm{i}^{\ell_i+\ell_{i'}-\lambda}=\pm1$, since it follows from (A.27) that $(\ell_i0\lambda0|\ell_{i'}0)=0$ unless $\ell_i+\ell_{i'}-\lambda$ is even. It also follows from (D.12) that $\alpha^{\Gamma}_{ii'\lambda}$ is real and from (D.1) that $\alpha^{\Gamma}_{ii'\lambda}$ is symmetric so that $\alpha^{\Gamma}_{ii'\lambda}=\alpha^{\Gamma}_{i'i\lambda}$.

We next derive an explicit expression for the long-range potential coefficients when we adopt the Condon–Shortley phase convention. We again commence from (D.1), but we now expand $P_\lambda(\cos\theta_{kN+1})$ in terms of spherical harmonics using (B.48) which we rewrite here as

$$P_\lambda(\cos\theta_{kN+1}) = \frac{4\pi}{2\lambda+1}\sum_{m=-\lambda}^{+\lambda}Y_{\lambda m}(\theta_k,\phi_k)Y^*_{\lambda m}(\theta_{N+1},\phi_{N+1}), \tag{D.13}$$

and we define the channel function $\overline{\Phi}^{\Gamma}_i$ in (D.1) as follows

$$\begin{aligned}\overline{\Phi}^{\Gamma}_i(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1}) &= \sum_{M_{L_i}m_{\ell_i}}\sum_{M_{S_i}m_i}(L_iM_{L_i}\ell_im_{\ell_i}|LM_L)\\ &\times(S_iM_{S_i}\tfrac{1}{2}m_i|SM_S)\Phi^{\mathrm{CS}}_i(\mathbf{X}_N)\\ &\times Y_{\ell_im_{\ell_i}}(\theta_{N+1},\phi_{N+1})\chi_{\frac{1}{2}m_i}(\sigma_{N+1}),\end{aligned} \tag{D.14}$$

and an analogous equation for $\overline{\Phi}^{\Gamma}_{i'}$. We also introduce the tensor operators

$$M^{\mathrm{CS}}_{\lambda m} = \left(\frac{4\pi}{2\lambda+1}\right)^{1/2}\sum_{k=1}^{N}r_k^{\lambda}Y_{\lambda m}(\theta_k,\phi_k) \tag{D.15}$$

and

$$C^{\mathrm{CS}}_{\lambda m} = \left(\frac{4\pi}{2\lambda+1}\right)^{1/2}Y_{\lambda m}(\theta_{N+1},\phi_{N+1}). \tag{D.16}$$

Substituting these results into (D.1) and carrying out the summations over the spin magnetic quantum numbers then give

$$\left(\alpha_{ii'\lambda}^{\Gamma}\right)^{\text{CS}} = \sum_{m} \sum_{M_{L_i} m_{\ell_i}} \sum_{M_{L_{i'}} m_{\ell_{i'}}} \langle \Phi_i^{\text{CS}}(\mathbf{X}_N) | M_{\lambda m}^{\text{CS}} | \Phi_{i'}^{\text{CS}}(\mathbf{X}_N) \rangle$$
$$\times \langle Y_{\ell_i m_{\ell_i}}(\theta_{N+1}, \phi_{N+1}) | C_{\lambda m}^{\text{CS}*} | Y_{\ell_{i'} m_{\ell_{i'}}}(\theta_{N+1}, \phi_{N+1}) \rangle$$
$$\times (L_i M_{L_i} \ell_i m_{\ell_i} | L M_L)(L_{i'} M_{L_{i'}} \ell_{i'} m_{\ell_{i'}} | L M_L) \delta_{S_i S_{i'}} . \quad \text{(D.17)}$$

The integration over the scattered electron angular coordinates $\hat{\mathbf{r}}_{N+1}$ in (D.17) can be carried out using (B.45) yielding

$$\langle Y_{\ell_i m_{\ell_i}}(\theta_{N+1}, \phi_{N+1}) | C_{\lambda m}^{\text{CS}*} | Y_{\ell_{i'} m_{\ell_{i'}}}(\theta_{N+1}, \phi_{N+1}) \rangle$$
$$= (-1)^m \left[\frac{2\ell_{i'} + 1}{2\ell_i + 1} \right]^{1/2} (\lambda - m \ell_{i'} m_{\ell_{i'}} | \ell_i m_{\ell_i})(\lambda 0 \ell_{i'} 0 | \ell_i 0), \quad \text{(D.18)}$$

and we introduce the reduced multipole moments of the target by the equation

$$\langle \Phi_i^{\text{CS}}(\mathbf{X}_N) | M_{\lambda m}^{\text{CS}} | \Phi_{i'}^{\text{CS}}(\mathbf{X}_N) \rangle = (2L_i + 1)^{-1/2} (L_{i'} M_{L_{i'}} \lambda m | L_i M_{L_i})$$
$$\times \langle \alpha_i L_i S_i \pi_i || M_{\lambda}^{\text{CS}} || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle . \quad \text{(D.19)}$$

Substituting (D.18) and (D.19) into (D.17) and collecting terms involving the orbital magnetic quantum numbers then yield the following summation

$$S = \sum_{m} \sum_{M_{L_i} m_{\ell_i}} \sum_{M_{L_{i'}} m_{\ell_{i'}}} (-1)^m (L_i M_{L_i} \ell_i m_{\ell_i} | L M_L)(L_{i'} M_{L_{i'}} \ell_{i'} m_{\ell_{i'}} | L M_L)$$
$$\times (\lambda - m \ell_{i'} m_{\ell_{i'}} | \ell_i m_{\ell_i})(L_{i'} M_{L_{i'}} \lambda m | L_i M_{L_i}), \quad \text{(D.20)}$$

which is the same as (D.9) and can thus be evaluated yielding (D.11). Substituting this result into (D.17) then gives the following expression for the long-range potential coefficients using the Condon–Shortley phase convention

$$\left(\alpha_{ii'\lambda}^{\Gamma}\right)^{\text{CS}} = (-1)^{L_i + \ell_i - L} (2\ell_i + 1)^{1/2} (\ell_i 0 \lambda 0 | \ell_{i'} 0) W(L_i L_{i'} \ell_i \ell_{i'}; \lambda L)$$
$$\times \langle \alpha_i L_i S_i \pi_i || M_{\lambda}^{\text{CS}} || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle \delta_{S_i S_{i'}} . \quad \text{(D.21)}$$

Comparing this result with (D.12) we see that the Condon–Shortley reduced multipole matrix element is replaced by the equivalent Fano–Racah matrix element and the overall phase factor is modified, although in both cases $\alpha_{ii'\lambda}^{\Gamma}$ is real and symmetric. Hence, as pointed out in the introduction to this appendix, a consistent phase convention must be adopted throughout the analysis in order to obtain correct results for the physical observables.

D.1.2 Inclusion of Relativistic Effects

The above analysis has to be extended as the nuclear charge number Z increases and relativistic effects start to play an important role in low- and intermediate-energy electron collisions with atoms and atomic ions. In this section we derive explicit expressions for the long-range potential coefficients, using the Fano–Racah phase convention, when relativistic effects can be accurately described by the Breit–Pauli Hamiltonian discussed in Sect. 5.4.2.

We commence by deriving an expression for the long-range potential coefficients when relativistic effects in the target can be neglected. Adopting the pair-coupling scheme, defined by (5.116), we obtain the following expression for the long-range potential coefficients $\alpha_{ii'\lambda}^{J\pi}$ in terms of the long-range potential coefficients, $\alpha_{ii'\lambda}^{\Gamma}$ defined by (D.1) in the absence of relativistic effects,

$$\alpha_{ii'\lambda}^{J\pi} = \sum_{LS} \langle [(L_i S_i)J_i, \ell_i]K_i \tfrac{1}{2}; JM_J | (L_i \ell_i)L, (S_i \tfrac{1}{2})S; JM_J \rangle \\ \times \alpha_{ii'\lambda}^{\Gamma} \langle (L_{i'} \ell_{i'})L, (S_{i'} \tfrac{1}{2})S; JM_J | [(L_{i'} S_{i'})J_{i'}, \ell_{i'}]K_{i'} \tfrac{1}{2}; JM_J \rangle . \quad \text{(D.22)}$$

We see that the transformation in this equation has the same form as the transformation of the K-matrix defined by (5.119). We can carry out the summation over L and S in (D.22) using the expression for the recoupling coefficients in terms of Racah coefficients given by (5.118) and for the long-range potential coefficient $\alpha_{ii'\lambda}^{\Gamma}$ given by (D.12). After using the orthogonality relation and the sum rule satisfied by the Racah coefficients, given by (A.50) and (A.52), we find that (D.22) reduces to

$$\alpha_{ii'\lambda}^{J\pi} = \mathrm{i}^{\ell_i + \ell_{i'} - \lambda} (-1)^{L_{i'} + S_i - K_i - \lambda} [(2\ell_i + 1)(2J_i + 1)(2J_{i'} + 1)]^{1/2} \\ \times (\ell_i 0 \lambda 0 | \ell_{i'} 0) W(\ell_i J_i \ell_{i'} J_{i'}; K_i \lambda) W(L_i J_i L_{i'} J_{i'}; S_i \lambda) \\ \times \langle \alpha_i L_i S_i \pi_i || M_\lambda^{\mathrm{FR}} || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle \delta_{S_i S_{i'}} \delta_{K_i K_{i'}} . \quad \text{(D.23)}$$

This equation can be further simplified by introducing the following reduced multipole moments corresponding to the fine-structure levels of the target

$$\langle \alpha_i L_i S_i J_i \pi_i || M_\lambda^{\mathrm{FR}} || \alpha_{i'} L_{i'} S_{i'} J_{i'} \pi_{i'} \rangle \\ = (-1)^{L_{i'} + \overline{S}_i - \lambda} [(2J_i + 1)(2J_{i'} + 1)]^{1/2} W(L_i J_i L_{i'} J_{i'}; S_i \lambda) \\ \times \langle \alpha_i L_i S_i \pi_i || M_\lambda^{\mathrm{FR}} || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle \delta_{S_i S_{i'}} , \quad \text{(D.24)}$$

where the reduced multipole moment on the right-hand side of this equation is defined by (D.8). The expression (D.23) for the long-range potential coefficients then becomes

$$\alpha^{J\pi}_{ii'\lambda} = \mathrm{i}^{\ell_i+\ell_{i'}-\lambda}(-1)^{-\overline{K}_i}(2\ell_i+1)^{1/2}(\ell_i 0\lambda 0|\ell_{i'}0)W(\ell_i J_i \ell_{i'} J_{i'}; K_i\lambda)$$
$$\times \langle \alpha_i L_i S_i J_i \pi_i || M^{\mathrm{FR}}_{\lambda} || \alpha_{i'} L_{i'} S_{i'} J_{i'} \pi_{i'} \rangle \delta_{K_i K_{i'}}. \tag{D.25}$$

In (D.24) and (D.25) we have introduced the quantities $\overline{S}_i$ and $\overline{K}_i$ which are the integral parts of S_i and K_i, respectively, so that $\overline{S}_i - \overline{K}_i = S_i - K_i$. This ensures that the transformed reduced multipole moments of the target $\langle \alpha_i L_i S_i J_i \pi_i || M^{\mathrm{FR}}_{\lambda} || \alpha_{i'} L_{i'} S_{i'} J_{i'} \pi_{i'} \rangle$ defined by (D.24) are real. It follows from (D.24) and (D.25) that the long-range potential coefficients are diagonal in the quantum numbers S_i and K_i.

When relativistic effects in the target are important then the long-range potential coefficients must be transformed using the term-coupling coefficients $f(\Delta_i J_i \pi_i; \alpha_i L_i S_i \pi_i)$ defined by (5.122). The transformed long-range potential coefficients are then given by

$$\alpha^{J\pi}_{\mu\mu'\lambda} = \sum_{\alpha_i L_i S_i} \sum_{\alpha_{i'} L_{i'} S_{i'}} f(\Delta_i J_i \pi_i; \alpha_i L_i S_i \pi_i) \alpha^{J\pi}_{ii'\lambda} f(\Delta_{i'} J_{i'} \pi_{i'}; \alpha_{i'} L_{i'} S_{i'} \pi_{i'}), \tag{D.26}$$

where the channel subscripts μ and μ' on the coefficients $\alpha^{J\pi}_{\mu\mu'\lambda}$ are defined by

$$\mu \equiv \Delta_i \; J_i \; \ell_i \; K_i \; \tfrac{1}{2}, \quad \mu' \equiv \Delta_{i'} \; J_{i'} \; \ell_{i'} \; K_{i'} \; \tfrac{1}{2}. \tag{D.27}$$

The summation over S_i and $S_{i'}$ in (D.26) means that the transformed long-range potential coefficients are no longer diagonal in the spin quantum number S_i. However, it follows from (D.25) and (D.26) that these coefficients are still diagonal in the quantum number K_i. This conservation rule follows from the definition of the pair-coupling scheme given by (5.116). Since the total angular momentum quantum number J is conserved, and since the spin s_i of the scattered electron is also conserved in the external region, where electron exchange effects are zero, then the quantum number K_i is also conserved. As discussed in Sect. 5.4.2, conservation of K_i results in the coupled second-order differential equations, describing the radial motion of the scattered electron in the external and asymptotic regions, sub-dividing into two uncoupled sets of equations with considerable saving in computational effort.

In conclusion, we see from (D.12), (D.25) and (D.26) that the problem of calculating the long-range potential coefficients has been separated into two distinct parts: first, the calculation of the Clebsch–Gordan and Racah coefficients which depend on the target orbital angular momenta, the total angular momentum and λ and second, the calculation of the reduced multipole moments of the target which involves the detailed atomic structure of the target states.

D.2 *R*-Matrix–Floquet Multiphoton Potential

As our second application of angular momentum algebra theory, we derive explicit expressions for the long-range potential which arises in R-matrix–Floquet theory of atomic multiphoton processes, discussed in Sect. 9.1, where in this analysis and in later examples discussed in this appendix we adopt the Fano–Racah phase convention discussed in Appendix B.4. We have shown in Sect. 9.1.3 that this potential is defined by (9.41) as follows

$$\mathbf{W}^{\mathbf{V}\gamma} = \mathbf{V}^{E\gamma} + \mathbf{V}^{D\gamma} + \mathbf{V}^{P\gamma}. \tag{D.28}$$

We consider these three terms successively below.

First, $\mathbf{V}^{E\gamma}$ arises from the electron–electron and electron–nuclear potential terms in the Hamiltonian H_{N+1} defined by (5.3). Its matrix elements are defined by (9.42) as follows

$$V^{E\gamma}_{nLin'L'i'} = \langle r^{-1}_{N+1}\overline{\Phi}^{\gamma}_{nLi}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\left|\sum_{j=1}^{N}\frac{1}{r_{jN+1}} - \frac{N}{r_{N+1}}\right| \\ \times\, r^{-1}_{N+1}\overline{\Phi}^{\gamma}_{n'L'i'}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle'\delta_{nn'}, \tag{D.29}$$

where the integration in this equation is carried out over all the $(N+1)$-electron space and spin coordinates except the radial coordinate of the $(N+1)$th electron. Also the term $-N/r_{N+1}$ is included so that the long-range Coulomb interaction experienced by the ejected or scattered electron is completely included on the left-hand side of (9.38). Using expansion (B.49) for the $1/r_{jN+1}$ terms in (D.29) we obtain

$$V^{E\gamma}_{nLin'L'i'}(r) = \sum_{\lambda=1}^{\lambda_{\max}} \alpha^{\gamma}_{ii'\lambda} r^{-\lambda-1}\delta_{nn'}\delta_{LL'}, \quad r \ge a_0, \tag{D.30}$$

which is the same as the long-range potential arising in electron collisions with atoms and atomic ions defined by (2.73) and (2.74). An explicit expression for the real coefficients $\alpha^{\gamma}_{ii'\lambda}$ has been derived in Appendix D.1.1 and is given by (D.12) using the Fano–Racah phase convention, where we observe that in these expressions the total orbital angular momentum $L = L'$ is conserved. The potential $\mathbf{V}(r)$ in (9.61) is then given in terms of $\mathbf{V}^{E\gamma}$ by

$$\mathbf{V}(r) = -\frac{\boldsymbol{\ell}(\boldsymbol{\ell}+\mathbf{I})}{r^2} + \frac{2(Z-N)}{r}\mathbf{I} - 2\mathbf{V}^{E\gamma}(r), \tag{D.31}$$

where the first two terms on the right-hand side of this equation are diagonal matrices.

Next, the $\mathbf{V}^{D\gamma}$ term in (D.28) arises from the dipole length operator D_N in (9.34) which we write here using the Fano–Racah phase convention as

$$D_N = \frac{1}{2}\mathcal{E}_0 \sum_{i=1}^{N} z_i = -\mathrm{i}\mathcal{D}_N = -\frac{\mathrm{i}}{2}\left(\frac{4\pi}{3}\right)^{1/2} \mathcal{E}_0 \sum_{i=1}^{N} r_i \mathcal{Y}_{10}(\theta_i, \phi_i), \tag{D.32}$$

where we have taken the z-axis to lie along the laser polarization direction $\hat{\boldsymbol{\epsilon}}$. The matrix elements of D_N, defined by (9.43), are then given by

$$\begin{aligned} V^{D\gamma}_{nLin'L'i'} = \langle r^{-1}_{N+1} \overline{\Phi}^{\gamma}_{nLi}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) \,|D_N|\, r^{-1}_{N+1} \\ \times\, \overline{\Phi}^{\gamma}_{n'L'i'}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle' \left(\delta_{nn'-1} + \delta_{nn'+1}\right). \end{aligned} \tag{D.33}$$

We expand the channel functions $\overline{\Phi}^{\gamma}_{nLi}$ and $\overline{\Phi}^{\gamma}_{n'L'i'}$ in terms of the residual atom or ion states Φ_i and $\Phi_{i'}$ by an equation analogous to (D.3). The summation over the orbital magnetic quantum numbers in (D.33) can then be carried out by introducing the reduced dipole matrix elements of the target $\langle \alpha_i L_i S_i \pi_i || \mathcal{D}_N || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle$, in analogy with (D.8). That is, we write

$$\begin{aligned} \langle \Phi_i(\mathbf{X}_N)|\mathcal{D}_N|\Phi_{i'}(\mathbf{X}_N)\rangle = (2L_i+1)^{-1/2}(L_{i'} M_{L_{i'}} 10 | L_i M_{L_i}) \\ \times\, \langle \alpha_i L_i S_i \pi_i || \mathcal{D}_N || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle. \end{aligned} \tag{D.34}$$

Following the angular momentum algebra procedure adopted in the simplification of $\alpha^{\gamma}_{ii'\lambda}$ defined by (D.6) we find that (D.33) reduces to

$$\begin{aligned} V^{D\gamma}_{nLin'L'i'} &= -\mathrm{i}(-1)^{L_{i'}+\ell_i+L+L'+M_L+1}(\delta_{nn'-1} + \delta_{nn'+1}) \\ &\times \left[\frac{(2L+1)(2L'+1)}{3}\right]^{1/2} (LM_L L'\, -M_{L'}|10) W(LL_i L' L_{i'}; \ell_i 1) \\ &\times \langle \alpha_i L_i S_i \pi_i || \mathcal{D}_N || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle \delta_{\ell_i \ell_{i'}} \delta_{m_{\ell_i} m_{\ell_{i'}}} \delta_{M_L M_{L'}} \delta_{M_{L_i} M_{L_{i'}}} \\ &\times \delta_{S_i S_{i'}} \delta_{M_{S_i} M_{S_{i'}}} \delta_{SS'} \delta_{M_S M_{S'}} \delta_{m_i m_{i'}}. \end{aligned} \tag{D.35}$$

We see that the $\mathbf{V}^{D\gamma}$ term is independent of the radial coordinate r of the ejected or scattered electron and connects channels where

$$n = n' \pm 1, \quad L_i = L_{i'}, L_{i'} \pm 1, \quad \ell_i = \ell_{i'}, \quad L = L', L' \pm 1, \quad M_L = M_{L'} \tag{D.36}$$

and also where the spin quantum numbers are conserved.

The symmetry properties of $\mathbf{V}^{D\gamma}$ follow immediately from the symmetry relations satisfied by the Clebsch–Gordan and Racah coefficients in (D.35) and the following symmetry property of the reduced matrix element in this equation

$$\langle \alpha_i L_i S_i \pi_i || \mathcal{D}_N || \alpha_{i'} L_{i'} S_{i'} \pi_{i'} \rangle = \langle \alpha_{i'} L_{i'} S_{i'} \pi_{i'} || \mathcal{D}_N || \alpha_i L_i S_i \pi_i \rangle. \tag{D.37}$$

Also, this reduced matrix element can be shown to be real. Hence it follows that

$$\left(\mathbf{V}^{D\gamma}\right)^{\mathrm{T}} = -\mathbf{V}^{D\gamma} \quad \text{and} \quad \left(\mathbf{V}^{D\gamma}\right)^{\dagger} = \mathbf{V}^{D\gamma} \tag{D.38}$$

so that $\mathbf{V}^{D\gamma}$ is pure imaginary, antisymmetric, hermitian and independent of r. We also note that the potential $\mathbf{D}$ in (9.61) is given in terms of $\mathbf{V}^{D\gamma}$ by

$$\mathbf{D} = -2\mathbf{V}^{D\gamma}. \tag{D.39}$$

We observe that if instead of using the Fano–Racah phase convention for the spherical harmonics we had used the Condon–Shortley phase convention then $\mathbf{V}^{D\gamma}$ would have been real, symmetric and hermitian.

Finally, the $\mathbf{V}^{P\gamma}$ term in (D.28) arises from the dipole velocity operator P_{N+1} defined by (9.35). Its matrix elements are defined by (9.44) as follows:

$$\begin{aligned} V^{P\gamma}_{nLin'L'i'} = {} & \langle r^{-1}_{N+1} \overline{\Phi}^{\gamma}_{nLi}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) \left| \mathrm{i}\frac{A_0}{2\mathrm{c}} \hat{\boldsymbol{\epsilon}} \cdot \mathbf{p}_{N+1} \right| r^{-1}_{N+1} \\ & \times \overline{\Phi}^{\gamma}_{n'L'i'}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle' \left(\delta_{nn'+1} - \delta_{nn'-1}\right). \end{aligned} \tag{D.40}$$

In order to evaluate this expression we again take the z-axis to lie along the laser polarization direction $\hat{\boldsymbol{\epsilon}}$ so that $\hat{\boldsymbol{\epsilon}} \cdot \mathbf{p}$ is defined by (B.72). Also, we remember that the channel functions $\overline{\Phi}^{\gamma}_i$ are defined by (D.3) using the Fano–Racah phase convention and the matrix elements of $\hat{\boldsymbol{\epsilon}} \cdot \mathbf{p}$ in a spherical harmonic basis are given by (B.73). We then find after some angular momentum algebra that (D.40) reduces to

$$\begin{aligned} V^{P\gamma}_{nLin'L'i'} = {} & \frac{A_0}{2\mathrm{c}}(\delta_{nn'+1} - \delta_{nn'-1})\mathrm{i}^{\ell_{i'}-\ell_i}(-1)^{\ell_i+L-L_i}[(2\ell_i+1)(2L+1)]^{1/2} \\ & \times (\ell_i 010|\ell_{i'}0)(LM_L 10|L'M_L)W(L\ell_i L'\ell_{i'}; L_i 1) \\ & \times \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{f(\ell_{i'}, \ell_i)}{r} - \frac{1}{r}\right) \delta_{SS'}\delta_{M_S M_{S'}}\delta_{M_L M_{L'}}\delta_{L_i L_{i'}}\delta_{M_{L_i} M_{L_{i'}}} \\ & \times \delta_{S_i S_{i'}}\delta_{M_{S_i} M_{S_{i'}}}\delta_{m_{\ell_i} m_{\ell_{i'}}}\delta_{m_i m_{i'}}, \end{aligned} \tag{D.41}$$

where $f(\ell_{i'}, \ell_i)$ is defined by (B.70) with the primed and unprimed quantities interchanged. In addition, following our analysis of (B.74), we observe that the $1/r$ term in the brackets in (D.41) arises from the operation of $\hat{\boldsymbol{\epsilon}} \cdot \mathbf{p}_{N+1}$ in (D.40) on the radial wave function $r^{-1} F^{\mathbf{V}\gamma}_{nLij}(r)$, where the reduced radial wave function $F^{\mathbf{V}\gamma}_{nLij}(r)$ satisfies (9.38). Hence we find that $V^{E\gamma}_{nLin'L'i'}$ defined by (9.42), operates, as required, on the reduced radial wave function $F^{\mathbf{V}\gamma}_{nLij}(r)$ in (9.38).

The symmetry properties of $\mathbf{V}^{P\gamma}$ follow immediately from (D.41) and (B.70). Since $\ell_i = \ell_{i'} \pm 1$ in (D.41) then $\mathrm{i}^{\ell_{i'}-\ell_i} = \mp\mathrm{i}$, and since all other terms in this equation are real then $\mathbf{V}^{P\gamma}$ is pure imaginary. The potentials $\mathbf{P}$ and $\mathbf{Q}$ in (9.61) are defined in terms of $\mathbf{V}^{P\gamma}$ by

$$\mathbf{P}\frac{\mathrm{d}}{\mathrm{d}r} + \mathbf{Q}\frac{1}{r} = -2\mathbf{V}^{P\gamma}. \tag{D.42}$$

It then follows from (D.41) and (D.42) that $\mathbf{P}$ and $\mathbf{Q}$ are pure imaginary and independent of the radial coordinate r. It follows from the symmetry properties of the Clebsch–Gordan and Racah coefficients, given in Appendix A, and the symmetry of the function $f(\ell_{i'}, \ell_i)$, defined by (B.70), that

$$\mathbf{P}^{\mathrm{T}} = \mathbf{P} \quad \text{and} \quad \mathbf{Q}^{\mathrm{T}} = -\mathbf{Q}, \tag{D.43}$$

where $\mathbf{P}^{\mathrm{T}}$ and $\mathbf{Q}^{\mathrm{T}}$ are the transposes of $\mathbf{P}$ and $\mathbf{Q}$. Hence it follows that

$$\mathbf{P}^{\dagger} = -\mathbf{P} \quad \text{and} \quad \mathbf{Q}^{\dagger} = \mathbf{Q}, \tag{D.44}$$

where $\mathbf{P}^{\dagger}$ and $\mathbf{Q}^{\dagger}$ are the hermitian conjugates of $\mathbf{P}$ and $\mathbf{Q}$, respectively, so that $\mathbf{P}$ is antihermitian and $\mathbf{Q}$ is hermitian.

If instead of using the Fano–Racah phase convention for the spherical harmonics we had used the Condon–Shortley phase convention then both $\mathbf{P}$ and $\mathbf{Q}$ would have been real but (D.44) would still have been satisfied. In both cases it follows from (D.41) and (D.42) that the diagonal elements of $\mathbf{P}$ and $\mathbf{Q}$ are zero.

D.3 Time-Dependent Multiphoton Potential

As our third application of angular momentum algebra theory we derive explicit expressions for the long-range potential that arises in time-dependent R-matrix theory of atomic multiphoton processes, discussed in Sect. 10.1, using the Fano–Racah phase convention. We have shown in Sect. 10.1.3 that this potential is defined by (10.53) as follows:

$$\mathbf{W}^{\gamma} = \mathbf{V}^{E\gamma} + \mathbf{V}^{D\gamma} + \mathbf{V}^{P\gamma}, \tag{D.45}$$

where in the following analysis we will assume that the dipole velocity gauge is adopted. We now consider the three terms in (D.45) successively below.

First, $\mathbf{V}^{E\gamma}$ arises from the electron–electron and electron–nuclear potential terms in the Hamiltonian H_{N+1} defined by (5.3). Its matrix elements are given, in analogy with (D.29), by

$$V_{ii'}^{E\gamma} = \langle r_{N+1}^{-1}\overline{\Phi}_i^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\left|\sum_{j=1}^{N}\frac{1}{r_{jN+1}} - \frac{N}{r_{N+1}}\right| \times r_{N+1}^{-1}\overline{\Phi}_{i'}^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle', \tag{D.46}$$

where the integration in this equation is carried out over all the $(N+1)$-electron space and spin coordinates except the radial coordinate of the $(N+1)$th electron. Following our analysis in Appendix D.2, see (D.30), we obtain the following expression for this potential:

$$V_{ii'}^{E\gamma}(r) = \sum_{\lambda=1}^{\lambda_{\max}} \alpha_{ii'\lambda}^{\gamma} r^{-\lambda-1}, \quad r \geq a_0, \tag{D.47}$$

which is the same as the long-range potential arising in electron collisions with atoms and atomic ions defined by (2.73) and (2.74). The potential $\mathbf{V}(r)$ in (10.55) is then given in terms of $\mathbf{V}^{E\gamma}$ by

$$\mathbf{V}(r) = -\frac{\boldsymbol{\ell}(\boldsymbol{\ell}+\mathbf{I})}{r^2} + \frac{2(Z-N)}{r}\mathbf{I} - 2\mathbf{V}^{E\gamma}(r), \tag{D.48}$$

where the first two terms on the right-hand side of this equation are diagonal matrices.

The $\mathbf{V}^{D\gamma}$ and $\mathbf{V}^{P\gamma}$ terms in (D.45) arise from the dipole velocity operator term $\mathrm{c}^{-1}\mathbf{A}(t)\cdot\mathbf{P}_{N+1}$, which when $t = t_{m+\frac{1}{2}}$, can be written as

$$P = \frac{1}{\mathrm{c}}\sum_{i=1}^{N+1}\mathbf{A}(t_{m+\frac{1}{2}})\cdot\mathbf{p}_i = P_N + P_{N+1}, \tag{D.49}$$

where P_N arises from the laser interaction with the residual ion containing N electrons, defined by

$$P_N = \frac{1}{\mathrm{c}}\sum_{i=1}^{N}\mathbf{A}(t_{m+\frac{1}{2}})\cdot\mathbf{p}_i, \tag{D.50}$$

and P_{N+1} arises from the laser interaction with the ejected or scattered electron, defined by

$$P_{N+1} = \frac{1}{\mathrm{c}}\mathbf{A}(t_{m+\frac{1}{2}})\cdot\mathbf{p}_{N+1}. \tag{D.51}$$

We now consider the contribution to the potential from P_N and P_{N+1} in turn.

The matrix elements of the potential $\mathbf{V}^{D\gamma}$ in (D.45), which corresponds to the interaction of the laser with the residual ion, are given by

$$V_{ii'}^{D\gamma} = \langle r_{N+1}^{-1}\overline{\Phi}_i^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\,|P_N|\,r_{N+1}^{-1}\overline{\Phi}_{i'}^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle', \tag{D.52}$$

where, taking the z-axis to lie along the laser polarization direction $\hat{\boldsymbol{\epsilon}}$, we can write

$$P_N = -\frac{\mathrm{i}}{\mathrm{c}}A(t_{m+\frac{1}{2}})\sum_{j=1}^{N}\left(\cos\theta_j\frac{\partial}{\partial r_j} - \frac{\sin\theta_j}{r_j}\frac{\partial}{\partial\theta_j}\right), \tag{D.53}$$

which follows from (B.72). Hence we can write

$$V_{ii'}^{D\gamma} = V_{ii'}^{D_1\gamma} + V_{ii'}^{D_2\gamma}, \tag{D.54}$$

where

$$V_{ii'}^{D_1\gamma} = -\frac{\mathrm{i}}{\mathrm{c}}A(t_{m+\frac{1}{2}})\langle r_{N+1}^{-1}\overline{\Phi}_i^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\left|\sum_{j=1}^{N}\cos\theta_j\frac{\partial}{\partial r_j}\right| \times r_{N+1}^{-1}\overline{\Phi}_{i'}^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle' \tag{D.55}$$

and

$$V_{ii'}^{D_2\gamma} = \frac{\mathrm{i}}{\mathrm{c}}A(t_{m+\frac{1}{2}})\langle r_{N+1}^{-1}\overline{\Phi}_i^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\left|\sum_{j=1}^{N}\frac{\sin\theta_j}{r_j}\frac{\partial}{\partial\theta_j}\right| \times r_{N+1}^{-1}\overline{\Phi}_{i'}^{\gamma}(\mathbf{X}_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle'. \tag{D.56}$$

In order to evaluate $V_{ii'}^{D_1\gamma}$, defined by (D.55), we expand the channel functions $\overline{\Phi}_i^{\gamma}$ and $\overline{\Phi}_{i'}^{\gamma}$ in terms of the residual atom or ion states Φ_i and $\Phi_{i'}$ using (D.3) with Γ replaced by γ. Also, it follows from (B.54) and (B.64) that

$$\cos\theta = -\mathrm{i}\left(\frac{4\pi}{3}\right)^{1/2}\mathcal{Y}_{10}(\theta,\phi), \tag{D.57}$$

and we define the reduced matrix element $\langle\alpha_i L_i S_i\pi_i||P_N^{(1)}||\alpha_{i'}L_{i'}S_{i'}\pi_{i'}\rangle$, in analogy with (D.34), as

$$\langle\Phi_i(\mathbf{X}_N)\left|\sum_{j=1}^{N}\mathcal{Y}_{10}(\theta_j,\phi_j)\frac{\partial}{\partial r_j}\right|\Phi_{i'}(\mathbf{X}_N)\rangle = (2L_i+1)^{-1/2}(L_{i'}M_{L_{i'}}10|L_iM_{L_i})\langle\alpha_i L_i S_i\pi_i||P_N^{(1)}||\alpha_{i'}L_{i'}S_{i'}\pi_{i'}\rangle. \tag{D.58}$$

In order to evaluate $V_{ii'}^{D_2\gamma}$, defined by (D.56), we again expand the channel functions $\overline{\Phi}_i^\gamma$ and $\overline{\Phi}_{i'}^\gamma$ in terms of the residual atom or ion states Φ_i and $\Phi_{i'}$ using (D.3) with Γ replaced by γ. Also, it follows from (B.40) and (B.64) that

$$\sin\theta \frac{\partial}{\partial\theta} Y_{\ell m}(\theta,\phi) = -\mathrm{i}a(\ell,m)\mathcal{Y}_{\ell+1m}(\theta,\phi) - \mathrm{i}b(\ell,m)\mathcal{Y}_{\ell-1m}(\theta,\phi), \tag{D.59}$$

where

$$a(\ell,m) = \ell\left[\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}\right]^{1/2} \tag{D.60}$$

and

$$b(\ell,m) = (\ell+1)\left[\frac{(\ell+m)(\ell-m)}{(2\ell-1)(2\ell+1)}\right]^{1/2}, \tag{D.61}$$

and where we have included the operation of $\sin\theta\,\partial/\partial\theta$ in (D.56) on the angular function $\mathcal{Y}_{\ell m}(\theta,\phi)$ in $\overline{\Phi}_{i'}^\gamma$. Hence we see that the operation of $\sin\theta\,\partial/\partial\theta$ in (D.56) modifies the orbital angular momenta of the residual ion by ±1 while leaving the magnetic quantum numbers unaltered. It follows that we can define the reduced matrix element $\langle\alpha_i L_i S_i \pi_i||P_N^{(2)}||\alpha_{i'} L_{i'} S_{i'} \pi_{i'}\rangle$ by

$$\begin{aligned}
&\langle\Phi_i(\mathbf{X}_N)\left|-\sum_{j=1}^{N}\frac{\sin\theta_j}{r_j}\frac{\partial}{\partial\theta_j}\right|\Phi_{i'}(\mathbf{X}_N)\rangle \\
&= -\mathrm{i}\left(\frac{4\pi}{3}\right)^{1/2}(2L_i+1)^{-1/2}\sum_{L_{i''}}(L_{i''}M_{L_{i'}}10|L_iM_{L_i}) \\
&\quad\times\langle\alpha_i L_i S_i \pi_i||P_N^{(2)}||\alpha_{i'} L_{i''} S_{i'} \pi_{i'}\rangle,
\end{aligned} \tag{D.62}$$

where, by comparing this result with (D.58), we see that there is an additional summation over $L_{i''}$, corresponding to the terms on the right-hand side of (D.59). Also, we have included the factor $-\mathrm{i}(4\pi/3)^{1/2}$ in (D.62) which corresponds to the factor in (D.57) used to transform (D.55). We then obtain after some angular momentum algebra that the matrix elements of $V_{ii'}^{D\gamma}$, defined by (D.54), (D.55) and (D.56), can be written in terms of the reduced matrix elements, defined by (D.58) and (D.62), as follows:

$$V_{ii'}^{D\gamma} = \frac{1}{c}\left(\frac{4\pi}{3}\right)^{1/2} A(t_{m+\frac{1}{2}})(-1)^{L'+\ell_i}(2L+1)^{1/2}(LM_L 10|L'M_L)$$
$$\times \sum_{L_{i''}} \Big[W(LL_i L' L_{i''}; \ell_i 1)\langle \alpha_i L_i S_i \pi_i || P_N^{(1)} || \alpha_{i'} L_{i''} S_{i'} \pi_{i'} \rangle (-1)^{L_{i''}} \delta_{L_{i'} L_{i''}}$$
$$+ W(LL_i L' L_{i''}; \ell_i 1)\langle \alpha_i L_i S_i \pi_i || P_N^{(2)} || \alpha_{i'} L_{i''} S_{i'} \pi_{i'} \rangle (-1)^{L_{i''}} \Big]$$
$$\times \delta_{M_L M_{L'}} \delta_{M_{L_i} M_{L_{i'}}} \delta_{SS'} \delta_{M_S M_{S'}} \delta_{S_i S_{i'}} \delta_{M_{S_i} M_{S_{i'}}} \delta_{\ell_i \ell_{i'}} \delta_{m_{\ell_i} m_{\ell_{i'}}} \delta_{m_i m_{i'}}. \tag{D.63}$$

We see that $V_{ii'}^{D\gamma}$ is independent of the radial coordinate of the ejected or scattered electron and connects channels where

$$L = L', \quad L' \pm 1, \quad M_L = M_{L'}, \tag{D.64}$$

and where the spin quantum numbers are conserved. The reduced matrix elements in (D.63) can be shown to be antisymmetric and hence $\mathbf{V}^{D\gamma}$ is real, symmetric, hermitian and independent of r. We also note that the potential $\mathbf{D}$ in (10.55) is given in terms of $\mathbf{V}^{D\gamma}$ by

$$\mathbf{D} = -2\mathbf{V}^{D\gamma}. \tag{D.65}$$

Finally, we consider the matrix elements of $\mathbf{V}^{P\gamma}$ in (D.45), corresponding to the interaction of the laser with the ejected or scattered electron. In this case the matrix elements are given by

$$V_{ii'}^{P\gamma} = \langle r_{N+1}^{-1} \overline{\Phi}_i^{\gamma}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1}) \,|P_{N+1}|\, r_{N+1}^{-1} \overline{\Phi}_{i'}^{\gamma}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}\sigma_{N+1})\rangle', \tag{D.66}$$

where P_{N+1} is defined by (D.51). After taking the z-axis to lie along the laser polarization direction $\hat{\boldsymbol{\epsilon}}$, we can write

$$P_{N+1} = -\frac{i}{c} A(t_{m+\frac{1}{2}}) \left(\cos\theta_{N+1} \frac{\partial}{\partial r_{N+1}} - \frac{\sin\theta_{N+1}}{r_{N+1}} \frac{\partial}{\partial \theta_{N+1}} \right). \tag{D.67}$$

We then expand the channel functions $\overline{\Phi}_i^{\gamma}$ and $\overline{\Phi}_{i'}^{\gamma}$ in (D.66) in terms of the residual atom or ion states Φ_i and $\Phi_{i'}$ using (D.3) with Γ replaced by γ, and we use (B.72) and (B.73) to write

$$\langle \mathcal{Y}_{\ell m}(\theta,\phi) | P_{N+1} | \mathcal{Y}_{\ell' m'}(\theta,\phi) \rangle$$
$$= \frac{1}{c} A(t_{m+\frac{1}{2}}) i^{\ell'-\ell-1} \left[\frac{2\ell'+1}{2\ell+1} \right] (10\ell' m|\ell m)(10\ell' 0|\ell 0) \left(\frac{d}{dr_{N+1}} - \frac{f(\ell',\ell)}{r_{N+1}} \right)$$
$$\times \delta_{mm'}, \tag{D.68}$$

where $f(\ell', \ell)$ is defined by (B.70) with the primed and unprimed quantities interchanged. Using these results we then obtain after some angular momentum algebra that (D.66) reduces to

$$V_{ii'}^{P\gamma} = -\frac{\mathrm{i}}{\mathrm{c}} A(t_{m+\frac{1}{2}}) \mathrm{i}^{\ell_i' - \ell_i} (-1)^{\ell_i + L - L_i} \left[(2\ell_i + 1)(2L + 1)\right]^{1/2}$$
$$\times (\ell_i 010|\ell_{i'}0)(LM_L 10|L'M_L) W(L\ell_i L'\ell_{i'}; L_i 1) \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{f(\ell_{i'}, \ell_i)}{r} - \frac{1}{r}\right)$$
$$\times \delta_{SS'} \delta_{M_S M_{S'}} \delta_{M_L M_{L'}} \delta_{L_i L_i'} \delta_{M_{L_i} M_{L_{i'}}} \delta_{S_i S_{i'}} \delta_{M_{S_i} M_{S_{i'}}} \delta_{m_i m_{i'}} \delta_{m_{\ell_i} m_{\ell_{i'}}} . \tag{D.69}$$

We see that (D.69) has a similar form to (D.41), which arises in R-matrix–Floquet theory in Chap. 9. Also, it follows from the Clebsch–Gordan coefficients that the potential $V_{ii'}^{P\gamma}$ connects channels where

$$\ell_i = \ell_{i'} \pm 1, \quad L = L', \; L' \pm 1. \tag{D.70}$$

By comparing $\mathbf{V}^{P\gamma}$ with the potentials in (10.55) we find that

$$\mathbf{P}\frac{\mathrm{d}}{\mathrm{d}r} + \mathbf{Q}\frac{1}{r} = -2\mathbf{V}^{P\gamma}. \tag{D.71}$$

Also both $\mathbf{P}$ and $\mathbf{Q}$ are real since the factor $\mathrm{i}^{\ell_i' - \ell_i + 1}$ in (D.69) is real. In addition, it can be shown from (D.69) that $\mathbf{P}$ is antisymmetric, and hence antihermitian and $\mathbf{Q}$ is symmetric and hence hermitian so that

$$\mathbf{P}^{\mathrm{T}} = -\mathbf{P} \quad \text{and} \quad \mathbf{Q}^{\mathrm{T}} = \mathbf{Q}. \tag{D.72}$$

D.4 Atomic Photoionization Cross Section

In our final application of angular momentum algebra theory we derive an explicit expression for the differential photoionization cross section given in Sect. 8.1.1 by (8.43) and (8.44). In that section we obtained the following result for the differential cross section for photoionization of an unpolarized atom or ion by a polarized photon beam, see (8.41),

$$\frac{\mathrm{d}\sigma_{ij}^{V,L}}{\mathrm{d}\Omega} = \frac{A_{V,L}}{(2L+1)(2S+1)} \sum_{M_L M_S} \sum_{M_{L'} M_{S'}} \sum_{m_j'} |\langle \Psi_{jE}^- | D_\mu | \Psi_{iB} \rangle|^2, \tag{D.73}$$

where $A_{V,L}$ is a constant defined by (8.42) and where we write $\langle \Psi_{jE}^- | D_\mu | \Psi_{iB} \rangle$ in terms of the reduced matrix element $\langle \alpha_j' L_j' S_j' \ell_j' L' S' || D || \alpha_i L S \rangle$, defined by (8.38) as follows, see (8.40),

$$\langle \Psi_{jE}^- | D_\mu | \Psi_{iB} \rangle = \sum_{\ell'_j m_{\ell'_j}} \sum_{L'S'} (L'_j M_{L'_j} \ell'_j m_{\ell'_j} | L' M_{L'})(S'_j M_{S'_j} \tfrac{1}{2} m'_j | S' M_{S'})$$
$$\times (L M_L 1 \mu | L' M_{L'})(2L'+1)^{-1/2}(-\mathrm{i})^{\ell'_j} \exp(\mathrm{i}\sigma_{\ell'_j}) \mathcal{Y}_{\ell'_j m_{\ell'_j}}(\theta_k, \phi_k)$$
$$\times \langle \alpha'_j L'_j S'_j \ell'_j L' S' || D || \alpha_i L S \rangle \delta_{SS'} \delta_{M_S M_{S'}}. \tag{D.74}$$

We now substitute (D.74) into (D.73) yielding

$$\frac{\mathrm{d}\sigma_{ij}^{V,L}}{\mathrm{d}\Omega} = \frac{A_{V,L}}{(2L+1)(2S+1)}$$
$$\times \sum_{M_L M_S} \sum_{M_{L'} M_{S'}} \sum_{\ell'_j m_{\ell'_j} L'} \sum_{\ell''_j m_{\ell''_j} L''} \sum_{m'_j} [(2L'+1)(2L''+1)]^{-1/2}$$
$$\times \mathrm{i}^{\ell'_j - \ell''_j} \exp(-\mathrm{i}\sigma_{\ell'_j} + \mathrm{i}\sigma_{\ell''_j}) \mathcal{Y}^*_{\ell'_j m_{\ell'_j}}(\theta_k, \phi_k) \mathcal{Y}_{\ell''_j m_{\ell''_j}}(\theta_k, \phi_k)$$
$$\times (L'_j M_{L'_j} \ell'_j m_{\ell'_j} | L' M_{L'})(L'_j M_{L'_j} \ell''_j m_{\ell''_j} | L'' M_{L''})(S'_j M_{S'_j} \tfrac{1}{2} m'_j | S M_S)$$
$$\times (S'_j M_{S'_j} \tfrac{1}{2} m'_j | S M_S)(L M_L 1 \mu | L' M_{L'})(L M_L 1 \mu | L'' M_{L''})$$
$$\times \langle \alpha'_j L'_j S'_j \ell'_j L' S || D || \alpha_i L S \rangle^* \langle \alpha'_j L'_j S'_j \ell''_j L'' S || D || \alpha_i L S \rangle. \tag{D.75}$$

In order to simplify (D.75) we first observe from (A.16), satisfied by the Clebsch–Gordan coefficients, that

$$M_{L'} = M_{L''} \quad \text{and} \quad m_{\ell'_j} = m_{\ell''_j}. \tag{D.76}$$

Also, the summation over the spin magnetic quantum numbers M_S, $M_{S'}$ and m'_j in (D.75) can be carried out using (A.18) yielding a factor $(2S+1)$. We then use the following result satisfied by the Fano–Racah spherical harmonics:

$$\mathcal{Y}^*_{\ell'_j m_{\ell'_j}}(\theta_k, \phi_k) \mathcal{Y}_{\ell''_j m_{\ell''_j}}(\theta_k, \phi_k)$$
$$= \mathrm{i}^{-\ell'_j + \ell''_j} (-1)^{m_{\ell'_j}} \sum_{\ell} (4\pi)^{-1} [(2\ell'_j+1)(2\ell''_j+1)]^{1/2} (\ell'_j - m_{\ell'_j} \ell''_j m_{\ell''_j} | \ell 0)$$
$$\times (\ell'_j 0 \ell''_j 0 | \ell 0) P_\ell(\cos\theta_k), \tag{D.77}$$

which follows from (B.33), (B.38), (B.47) and (B.64). We also use (A.45) and the symmetry relations given by (A.21), (A.22), (A.23), (A.24), (A.25), and (A.26) to carry out the following summations over Clebsch–Gordan coefficients in (D.75):

$$\sum_{m_{\ell'_j}} (-1)^{m_{\ell'_j}} (L'_j M_{L'_j} \ell'_j m_{\ell'_j} | L' M_{L'}) (L'_j M_{L'_j} \ell''_j m_{\ell'_j} | L'' M_{L''}) (\ell'_j - m_{\ell'_j} \ell''_j m_{\ell'_j} | \ell 0)$$
$$= (-1)^{L'_j + M_{L'}} [(2L'+1)(2L''+1)]^{1/2} (L' M_{L'} L'' - M_{L'} | \ell 0)$$
$$\times W(L' \ell'_j L'' \ell''_j; L'_j \ell) \tag{D.78}$$

and

$$\sum_{M_L M_{L'}} (-1)^{M_{L'}} (L M_L 1 \mu | L' M_{L'}) (L M_L 1 \mu | L'' M_{L'}) (L' M_{L'} L'' - M_{L'} | \ell 0)$$
$$= (-1)^{L+\mu} [(2L'+1)(2L''+1)]^{1/2} (1 - \mu 1 \mu | \ell 0) W(1 L' 1 L''; L \ell). \tag{D.79}$$

Using (D.76), (D.77) and (D.78) we find that (D.75) can be rewritten in the form

$$\frac{d\sigma_{ij}^{V,L}}{d\Omega} = \frac{A_{V,L}}{4\pi(2L+1)} \sum_{\ell} A_\ell(\mu) P_\ell(\cos\theta_k), \tag{D.80}$$

where

$$A_\ell(\mu) = \sum_{L' L'' \ell'_j \ell''_j} (-1)^{L + L'_j + \mu} \exp(-i\sigma_{\ell'_j} + i\sigma_{\ell''_j}) \left[(2\ell'_j + 1)(2\ell''_j + 1)\right]^{1/2}$$
$$\times \left[(2L'+1)(2L''+1)\right]^{1/2} (1 - \mu 1 \mu | \ell 0)(\ell'_j 0 \ell''_j 0 | \ell 0)$$
$$\times W(L' \ell'_j L'' \ell''_j; L'_j \ell) W(1 L' 1 L''; L \ell)$$
$$\times \langle \alpha'_j L'_j S'_j \ell'_j L' S || D || \alpha_i L S \rangle^* \langle \alpha'_j L'_j S'_j \ell''_j L'' S || D || \alpha_i L S \rangle. \tag{D.81}$$

This result for the differential photoionization cross section was used in Sect. 8.1.1 to obtain expressions for the integrated photoionization cross section and the asymmetry parameter.