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On the consistency of Rabi frequency calculations

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Abstract. Three methods of calculating the on-resonance Rabi frequency for an atomic transition are described in detail. These methods are: the use of standard angular momentum coupling formula for state expansion; the application of the reduction formula for composite systems; and the application of reduction equations for vector operators from Condon and Shortley. It is shown that all three methods are equivalent, in contrast with previously reported difficulties in obtaining consistency in the phase. Each method is illustrated by calculating the Rabi frequencies for each hyperfine transition in a $n^2S_{1/2}$–$n'^2P_{3/2}$ manifold. The importance of consistency in the ordering of the quantum numbers in matrix elements of operator components is discussed.

1. Introduction

The Rabi frequency Ω is a measure of the strength of interaction between the dipole $\boldsymbol{D}$ associated with an atomic or molecular transition and the electric field $\boldsymbol{E}$ of exciting radiation, the relationship being defined as

$$\Omega = -\frac{\boldsymbol{D}\cdot\boldsymbol{E}}{\hbar}. \tag{1}$$

Ω is the cycling frequency as the system is driven repeatedly from the lower to the upper state of the transition and back again by absorption and stimulated emission of photons from resonant coherent radiation, such as that available from a single-mode laser. Coherent cyling at the Rabi frequency is interrupted randomly by non-coherent events, such as spontaneous emission or de-excitation due to collisions. The importance of the role of the Rabi frequency was acknowledged with the resurgence of research into atomic spectroscopy and the development of the fields of non-linear and quantum optics (see, for example, the review of Knight and Milonni [1] and references therein). The Rabi frequency for particular transitions has been observed in nutation signals in coherent optical transient experiments involving molecules [2] and atoms [3] as well as in the transient fluorescence of atomic lines [4].

Usually, an atomic transition under consideration has a manifold of energy states associated with it. The induced dipole matrix elements, and consequently the Rabi frequencies, between pairs of these substates will not necessarily be identical. In fact, not only is it possible that the values of these quantities vary considerably but also that their relative phase can differ by π. Thus, when calculating the response of such a transition to incident radiation, care must be taken to ensure accuracy in the sign of each Rabi frequency in the manifold so that the quantum interference of terms is accounted for correctly. An

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illustration of the requirements for such calculations has been seen in the modelling of substate populations of the sodium D2 line ($3^2S_{1/2}$–$3^2P_{3/2}$) excited by a single-mode field using a full quantum electrodynamic theory [5]. Because of the resolution of modern single-mode laser radiation, the energy levels associated with this line have to be written in the hyperfine interaction representation, resulting in 24 substates. Of course, due to selection rules, not all substates participate in a single-mode excitation. For example, with linearly-polarized light inducing π excitation from the $3^2S_{1/2}$ (F=2) ground state, there are 12 separate transitions and 17 participating substates.

The vectors of equation (1) are usually expressed in terms of a spherical basis [6] e_q ($q = -1, 0, 1$), defined in terms of the basis set for Cartesian space as

$$\begin{aligned} e_0 &= k \\ e_{\pm 1} &= \mp \frac{1}{\sqrt{2}}(i \pm \mathrm{i}j) \end{aligned} \tag{2}$$

so that, for example, D is expressed as

$$D = \sum_{q=-1}^{1} (-1)^q D_q e_{-q} \tag{3}$$

and similarly for E. Using equations (1)–(3), the Rabi frequency for a given excitation mode is found to be

$$\Omega_q = (-1)^{\frac{1}{2}q(1+q)+1} \sqrt{\frac{2I}{\varepsilon_0 c \hbar^2}} D_q \tag{4}$$

where $\sqrt{\frac{2I}{\varepsilon_0 c}}$ is the electric-field amplitude written in terms of the intensity I of the radiation after the amplitudes for circularly-polarized light have been chosen to give their standard form ($E_{\pm 1} = \mp E_C$) [6]. Thus, for a given transition between lower state $|F' m'_F\rangle$ and upper state $|F m_F\rangle$, the Rabi frequency is given by

$$\Omega(F, m_F, F', m'_F, q) = (-1)^{\frac{1}{2}q(1+q)+1} \sqrt{\frac{2I}{\varepsilon_0 c \hbar^2}} \langle F m_F | D_q | F' m'_F \rangle. \tag{5}$$

In the notation employed here, quantum numbers describing a state, such as the principal quantum number, which do not play an explicit role in the excitation process are not listed. From equation (5), the calculation of the Rabi frequency reduces to the evaluation of the dipole matrix element. This is achieved by expressing the matrix element in terms of a reduced matrix element common to all of the transitions in the manifold. The reduced matrix element can then be related to the Einstein A coefficient or relaxation rate between the levels of the reduced system. For the purposes of this work, we shall reduce the matrix elements to L representation.

D is an irreducible tensor operator of rank 1. We are aware of three methods for calculating matrix elements of components for such an operator. First, the element can be evaluated by the application of the standard angular momentum coupling formula followed by use of the Wigner–Eckart theorem. Second, the Wigner–Eckart theorem can be invoked initially, followed by the use of the reduction formula for composite systems [7, 8]. The

third method is to use the appropriate tables of Condon and Shortley [9]. On occasions, we have employed all of these methods to calculate Rabi frequencies for manifolds of transitions. However, up to now, we were not able to achieve consistency in the phase between the first two methods. At the same time, we recognize that there is a choice in sign for some terms in the tables of Condon and Shortley. As we have pointed out previously [10], if the calculations are being included in a model describing a single process, such as optical excitation of a transition, each method will yield the same value for an observable even with the difference in phase.

Problems do arise if there is more than one process being modelled, for example, as is the case for electron superelastic scattering in which optical excitation of the transition is followed by de-excitation by electron collision. The electron de-excitation process is described by a density matrix whose elements can only be evaluated by using standard angular momentum coupling formula since the density operator is not a vector. We have found that, if the Rabi frequencies required for the optical excitation step were calculated with the reduction formula for composite systems, the resulting expressions for the electron superelastic-scattering differential cross sections did not achieve agreement with previously stated results for simpler systems [11]. In particular, the optical pumping parameter for π excitation, K, was not identical to the line polarisation P_L of the resonance fluorescence from the excited state. In this case, for agreement, the Rabi frequencies had to be calculated by the standard angular momentum coupling formula method as well, which is the most time consuming of the three.

In this work, we report the resolution of the inconsistency between the three methods of calculating the Rabi frequency. In the next section, the derivation of the expressions for the Rabi frequency for a transition in hyperfine representation using the standard angular momentum coupling formula and the composite-system reduction formula methods will be presented and discussed. In section 3, the equivalence of the three methods of calculation will be established. Finally, in section 4, application of all three methods to a $n^2S_{1/2}$–$n'^2P_{3/2}$ transition will be undertaken and the results tabulated.

2. Methods of calculation

2.1. Standard angular momentum coupling formula

A state in hyperfine representation may be expanded as a sum of products of nuclear spin states and states in fine structure J represented by

$$|Fm_F\rangle = \sum_{m_I m_J} \langle I J m_I m_J | I J F m_F\rangle |I m_I\rangle |J m_J\rangle \tag{6}$$

where I is the nuclear spin quantum number and $\langle I J m_I m_J | I J F m_F\rangle$ is a Clebsch–Gordan coefficient. Throughout this paper, we shall use the higher-symmetry Wigner $3j$ symbol which is related to the Clebsch–Gordan coefficient by

$$\langle J_1 J_2 m_1 m_2 | J_1 J_2 J m\rangle = (-1)^{-J_1+J_2-m}\sqrt{2J+1}\begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & -m \end{pmatrix}. \tag{7}$$

Using equations (6) and (7), the dipole matrix element of equation (5) can be expanded as

$$\langle Fm_F|D_q|F'm'_F\rangle = \sum_{m_I m_J m'_I m'_J} (-1)^{-2I+J+J'-m_F-m'_F}\sqrt{(2F+1)(2F'+1)}$$
$$\times \begin{pmatrix} I & J & F \\ m_I & m_J & -m_F \end{pmatrix}\begin{pmatrix} I & J' & F' \\ m'_I & m'_J & -m'_F \end{pmatrix}\langle J m_J|D_q|J'm'_J\rangle\langle I m_I|I m'_I\rangle. \tag{8}$$

D does not operate on the nuclear spin, so the last factor is $\delta(m_I, m'_I)$ and the only non-zero term in the sum over m'_I is $m'_I = m_I$. The other summations are carried out explicitly using the limits imposed by the $3j$ symbols of $m_I = m_F - m_J = m'_F - m'_J$ and the limits of the magnetic quantum number $m_I = -I, \ldots, I$.

The states in the J representation are then expanded in terms of the electron spin states $|Sm_S\rangle$ and orbital angular momentum states $|Lm_L\rangle$ in a similar way, with D not operating on the electron spin

$$\langle Jm_J|D_q|J'm'_J\rangle = \sum_{m_S m_L m'_L} (-1)^{-2S+L+L'-m_J-m'_J}\sqrt{(2J+1)(2J'+1)}$$

$$\times \begin{pmatrix} S & L & J \\ m_S & m_L & -m_J \end{pmatrix}\begin{pmatrix} S & L' & J' \\ m_S & m'_L & -m'_J \end{pmatrix}\langle Lm_L|D_q|L'm'_L\rangle. \tag{9}$$

Once again, the summations are evaluated with $m_S = m_J - m_L = m'_J - m'_L$ and $m_S = -S, \ldots, S$. Next, the Wigner–Eckart theorem [7, 8] is applied to the matrix element $\langle Lm_L|D_q|L'm'_L\rangle$

$$\langle Lm_L|D_q|L'm'_L\rangle = (-1)^{L-m_L}\begin{pmatrix} L & 1 & L' \\ -m_L & q & m'_L \end{pmatrix}\langle L||D||L'\rangle. \tag{10}$$

The condition that the $3j$ symbol is zero if $m'_L + q \neq m_L$ imposes the selection rules for the magnetic substates. For π excitation, $m'_L = m_L$ and $q = 0$. Likewise, for σ^+ (σ^-) excitation, $q = 1$ ($q = -1$).

Finally, the reduced matrix element is evaluated via the relaxation rate Γ and wavelength λ of the transition as [7]

$$\langle L||D||L'\rangle = \sqrt{2L+1}\left(\frac{3\varepsilon_0\hbar\lambda^3\Gamma}{8\pi^2}\right)^{1/2}. \tag{11}$$

The result of the evaluation of the sequence of equations (8)–(11) is then substituted into equation (5) to produce the desired Rabi frequency value

$$\Omega(F, m_F, F', m'_F, q) = \sum_{m_I m_J m'_J m_S m_L m'_L} (-1)^{\frac{1}{2}q(1+q)+1-2I-2S+J+J'+2L+L'-m_F-m'_F-m_J-m'_J-m_L}$$

$$\times \sqrt{\frac{3\lambda^3\Gamma I}{4\pi^2 c\hbar}}\sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)(2L+1)}$$

$$\times \begin{pmatrix} I & J & F \\ m_I & m_J & -m_F \end{pmatrix}\begin{pmatrix} I & J' & F' \\ m_i & m'_J & -m'_F \end{pmatrix}\begin{pmatrix} S & L & J \\ m_S & m_L & -m_J \end{pmatrix}$$

$$\times \begin{pmatrix} S & L' & J' \\ m_S & m'_L & -m'_J \end{pmatrix}\begin{pmatrix} L & 1 & L' \\ -m_L & q & m'_L \end{pmatrix}. \tag{12}$$

2.2. Reduction formula for composite systems

In this method, the evaluation of reduced matrix elements follows from the theory of coupled angular momentum. If an irreducible tensor operator of rank k, U^k, commutes with angular momentum J_1 in the representation $J_1 J_2 J m_J$, then its reduced matrix element in this representation is found to be [7, 8]

$$\langle J_1 J_2 J||U^k||J_1 J_2' J'\rangle = (-1)^{J_1+J_2'+J+k}\langle J_2||U^k||J_2'\rangle\sqrt{(2J+1)(2J'+1)}\begin{Bmatrix} J_2 & J & J_1 \\ J' & J_2' & k \end{Bmatrix} \tag{13}$$

where any additional quantum numbers defining the states have been suppressed and

$$\begin{Bmatrix} J_2 & J & J_1 \\ J' & J_2' & k \end{Bmatrix}$$

is a Wigner $6j$ symbol. The procedure for evaluating the matrix element $\langle Fm_F|D_q|F'm_F'\rangle$ is then to first invoke the Wigner–Eckart theorem so that

$$\langle Fm_F|D_q|F'm_F'\rangle = (-1)^{F-m_F}\begin{pmatrix} F & 1 & F' \\ -m_F & q & m_F' \end{pmatrix}\langle F||D||F'\rangle. \tag{14}$$

We now write the reduced matrix element explicitly as $\langle IJF||D||IJ'F'\rangle$ where, as above, we assume that D commutes with I. Applying equation (13) yields

$$\langle IJF||D||IJ'F'\rangle = (-1)^{I+J'+F+1}\sqrt{(2F+1)(2F'+1)}\begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix}\langle J||D||J'\rangle. \tag{15}$$

Since D commutes with the electron spin S, the reduced matrix element in J representation can be evaluated in terms of a reduced matrix element in L representation, using equation (13) as

$$\langle SLJ||D||SL'J'\rangle = (-1)^{S+L'+J+1}\sqrt{(2J+1)(2J'+1)}\begin{Bmatrix} L & J & S \\ J' & L' & 1 \end{Bmatrix}\langle L||D||L'\rangle. \tag{16}$$

Equation (9.63) in Sobelman's book [7] is also an expression for $\langle SLJ||D||SL'J'\rangle$ which is identical in magnitude to equation (16) but differs in the exponent of -1 where $L+J'$ is written instead of $L'+J$. Since $L = L' \pm 1$ for a dipole transition, the sign of the two expressions could be different. A similar error could also arise in equation (15). We are of the opinion that, by using the correct form of the relation (equation (13)), the inconsistencies in the sign between the various methods of calculating the Rabi frequency has been resolved. In section 3, we shall show the equivalence of the three methods.

Combining equations (14)–(16) and (11) and substituting them into equation (5) yields an expression for the Rabi frequency

$$\begin{aligned}\Omega(F, m_F, F', m_F', q) = {} & (-1)^{\frac{1}{2}q(1+q)+1+2F-m_F+I+J'+S+L'+J}\sqrt{\frac{3\lambda^3\Gamma I}{4\pi^2 c\hbar}} \\ & \times\sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)(2L+1)} \\ & \times\begin{pmatrix} F & 1 & F' \\ -m_F & q & m_F' \end{pmatrix}\begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix}\begin{Bmatrix} L & J & S \\ J' & L' & 1 \end{Bmatrix}.\end{aligned} \tag{17}$$

3. Equivalence of methods

3.1. Standard angular momentum coupling formula and reduction formula for composite systems

In this section, the two methods described in section 2 will be shown to be formally equivalent. Consider the irreducible tensor operator U^k, which was introduced in equation (13). Application of the Wigner–Eckart theorem to the matrix element $\langle Jm_J|U^k_q|J'm'_J\rangle$ yields

$$\langle Jm_J|U^k_q|J'm'_J\rangle = (-1)^{J-m_J}\langle J||U^k||J'\rangle \begin{pmatrix} J & k & J' \\ -m_J & q & m'_J \end{pmatrix}. \tag{18}$$

Using equation (13), the matrix element can be expressed in terms of the reduced matrix element $\langle J_2||U^k||J'_2\rangle$ as

$$\langle J_1 J_2 J m_J|U^k_q|J_1 J'_2 J' m'_J\rangle = (-1)^{J_1+J'_2+2J+k-m_J}\langle J_2||U^k||J'_2\rangle\sqrt{(2J+1)(2J'+1)} \times \begin{pmatrix} J & k & J' \\ -m_J & q & m'_J \end{pmatrix} \begin{Bmatrix} J_2 & J & J_1 \\ J' & J'_2 & k \end{Bmatrix}. \tag{19}$$

Applying the angular momentum coupling formula of Section 2.1, followed by the Wigner–Eckart theorem, yields for the same matrix element

$$\langle J_1 J_2 J m_J|U^k_q|J_1 J'_2 J' m'_J\rangle = \sum_{m_1 m_2 m'_2} (-1)^{-2J_1+2J_2+J'_2-m_J-m'_J-m_2}\langle J_2||U^k||J'_2\rangle \times \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & -m_J \end{pmatrix} \begin{pmatrix} J_1 & J'_2 & J' \\ m_1 & m'_2 & -m'_J \end{pmatrix} \times \begin{pmatrix} J_2 & k & J'_2 \\ -m_2 & q & m'_2 \end{pmatrix}. \tag{20}$$

The sum of the product of the three $3j$ symbols in equation (20) can be put into standard form [7, 8] by making the following rearrangement using symmetry relations

$$\begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & -m_J \end{pmatrix} \begin{pmatrix} J_1 & J'_2 & J' \\ m_1 & m'_2 & -m'_J \end{pmatrix} \begin{pmatrix} J_2 & k & J'_2 \\ -m_2 & q & m'_2 \end{pmatrix} = (-1)^{J_2+J'_2+k} \begin{pmatrix} J & J_1 & J_2 \\ -m_J & m_1 & m_2 \end{pmatrix} \begin{pmatrix} J'_2 & k & J_2 \\ m'_2 & q & -m_2 \end{pmatrix} \begin{pmatrix} J'_2 & J_1 & J' \\ -m'_2 & m_1 & m'_J \end{pmatrix}. \tag{21}$$

For the product of the $3j$ symbols on the right-hand side of equation (21), the standard summation is

$$\sum_{m'_2 m_1 m_2} (-1)^{J'_2+J_1+J_2-m'_2+m_1-m_2} \begin{pmatrix} J & J_1 & J_2 \\ -m_J & m_1 & m_2 \end{pmatrix} \begin{pmatrix} J'_2 & k & J_2 \\ m'_2 & q & -m_2 \end{pmatrix} \begin{pmatrix} J'_2 & J_1 & J' \\ -m'_2 & m_1 & m'_J \end{pmatrix} = \begin{pmatrix} J & k & J' \\ -m_J & q & m'_J \end{pmatrix} \begin{Bmatrix} J & k & J' \\ J'_2 & J_1 & J_2 \end{Bmatrix} \tag{22}$$

where, by symmetry, the sums over m_2 and m'_2 are identical to those over $-m_2$ and $-m'_2$ respectively. After substitution of relationship (21) into equation (20), the argument of -1

is $-2J_1 + 3J_2 + 2J_2' - m_J - m_J' - m_2 + k$. This factor can be manipulated so that the exponent of -1 required for equation (22) is available

$$-2J_1 + 3J_2 + 2J_2' - m_J - m_J' - m_2 + k$$
$$= (-3J_1 + 2J_2 + J_2' - m_J - m_J' + k + m_2' - m_1) + (J_1 + J_2 + J_2' - m_2 - m_2' + m_1) \tag{23}$$

By recognizing that $m_1 + m_2' = m_J'$ and that $2(J_1 + m_1)$ is an even integer, the first bracket on the right-hand side of equation (23) becomes $-J_1 + 2J_2 + J_2' - m_J + k$. Therefore, after carrying out the summation in equation (20), the expression for the matrix element becomes

$$\langle J_1 J_2 J m_J | U_q^k | J_1 J_2' J' m_J' \rangle = (-1)^{-J_1 + 2J_2 + J_2' - m_J + k} \langle J_2 || U^k || J_2' \rangle \sqrt{(2J+1)(2J'+1)}$$
$$\times \begin{pmatrix} J & k & J' \\ -m_J & q & m_J' \end{pmatrix} \begin{Bmatrix} J & k & J' \\ J_2' & J_1 & J_2 \end{Bmatrix}. \tag{24}$$

After applying the appropriate symmetry rule for $6j$ symbols, it is clear that the magnitudes of equations (19) and (24) are identical and that they differ only in the exponent of -1. However, the exponents differ by $2(J_1 - J_2 + J)$, which, by the triangle condition, is an even integer. Thus, the signs of equations (19) and (24) are also the same. In section 2, the dipole matrix element in the F representation was reduced to L representation via the J representation. It is a straightforward extension of the procedure described here to prove the equivalence of equations (19) and (24) to show that the two methods of calculating the matrix element of section 2 produce identical results. For the two methods, the exponents of -1 differ by $2(S - L + J) + 2(I - J + F)$ which again is an even integer.

3.2. Reduction formula for composite systems and the tables of Condon and Shortley

The reduction formula for composite systems method and the tables of Condon and Shortley can be shown to be equivalent for each possible dipole matrix element. We shall illustrate the procedure with one specific case. All other cases were checked on a personal computer using available computer algebra software [12, 13].

The specific case chosen is the transition between a lower substate to an upper substate described by the change in quantum numbers $\Delta J = -1$, $\Delta m = -1$ (i.e. $q = -1$) and $\Delta J_2 = -1$ where $J = J_1 + J_2$ and D commutes with J_1. First, the Wigner–Eckart theorem is shown to be equivalent to equations $9^3 11$ of Condon and Shortley. For this transition, application of the Wigner–Eckart theorem yields

$$\langle Jm | D_{-1} | J+1 m+1 \rangle = (-1)^{J-m} \begin{pmatrix} J & 1 & J+1 \\ -m & -1 & m+1 \end{pmatrix} \langle J || D || J+1 \rangle. \tag{25}$$

The $3j$ symbol can be expressed algebraically from tables of standard formulae [7] resulting in

$$\langle Jm | D_{-1} | J+1 m+1 \rangle = \left[\frac{(J+m+1)(J+m+2)}{(2J+3)(2J+2)(2J+1)} \right]^{1/2} \langle J || D || J+1 \rangle. \tag{26}$$

D_{-1} is the magnitude of the relevant component of the vector D as defined by equation (3), whereas equations $9^3 11$ of Condon and Shortley are expressed as matrix elements of the vector. Equations (3) and (26) combine to give

$$\langle Jm | D | J+1 m+1 \rangle = \frac{1}{2} \left[\frac{(J+m+1)(J+m+2)}{(2J+3)(J+1)(2J+1)} \right]^{1/2} \langle J || D || J+1 \rangle (i + ij). \tag{27}$$

From the relevant equation of the set 9^311 of Condon and Shortley, the matrix element of the dipole vector operator for this transition is expressed as

$$\langle Jm|D|J+1m+1\rangle = -\tfrac{1}{2}[(J+m+1)(J+m+2)]^{1/2}\langle J\dot{:}D\dot{:}J+1\rangle(i+ij). \tag{28}$$

The Condon and Shortley reduced matrix element of the form $\langle J\dot{:}D\dot{:}J+1\rangle$ is related to the standard reduced matrix element by [7]

$$\langle J\dot{:}D\dot{:}J+1\rangle = \frac{-1}{[(J+1)(2J+1)(2J+3)]^{1/2}}\langle J||D||J+1\rangle. \tag{29}$$

Substituting equation (29) into equation (28) reproduces equation (27), thus confirming the equivalence of the Wigner–Eckart theorem and equations 9^311 of Condon and Shortley.

Next, the reduced matrix elements for this example are evaluated using each method. For the reduced formula for composite systems, equation (13) is applied to the matrix element

$$\langle J_1J_2J||D||J_1J_2+1J+1\rangle = (-1)^{J_1+J_2+J}[(2J+1)(2J+3)]^{1/2}\begin{Bmatrix} J_2 & J & J_1 \\ J+1 & J_2+1 & 1\end{Bmatrix}\langle J_2||D||J_2+1\rangle. \tag{30}$$

Expressing the $6j$ symbols algebraically [7] results in equation (30) becoming

$$\langle J_1J_2J||D||J_1J_2+1J+1\rangle = \left[\frac{(J_1+J+J_2+2)(J_1+J+J_2+3)(J+J_2-J_1+1)(J+J_2-J_1+2)}{(2J+2)(2J_2+1)(2J_2+2)(2J_2+3)}\right]^{1/2} \times \langle J_2||D||J_2+1\rangle. \tag{31}$$

In arriving at equation (31) from (30), the power of -1 is found to be $2(J_1+J_2+J)$. The sum of the three quantum numbers is an integer since they must satisfy the triangle rule. Therefore, the power of -1 is an even integer and the right-hand side of equation (31) is positive. To evaluate the reduced matrix element from Condon and Shortley, use is made of the appropriate expression in equations 11^38:

$$\langle J_1J_2J\dot{:}D\dot{:}J_1J_2+1J+1\rangle = \frac{1}{2(J+1)}\left[\frac{P(J+2)P(J+1)}{(2J+1)(2J+3)}\right]^{1/2}\langle J_2\dot{:}D\dot{:}J_2+1\rangle \tag{32}$$

where

$$P(J) = (J-J_1+J_2)(J+J_1+J_2+1). \tag{33}$$

Substitution of equation (33) into (32) and transforming to the standard reduced matrix elements using equation (29) reproduces equation (30). Hence, the evaluations of a dipole matrix element employing the reduction formula for composite systems and the equations of Condon and Shortley are also equivalent, ensuring the equivalence of all three methods of calculating the Rabi frequency.

4. Application

The three methods will be illustrated here by considering a specific example. Only the reduction formula for composite systems method results in the Rabi frequency for a transition being able to be expressed as a single-term equation. Inspection of equation (17) reveals that the expression for the Rabi frequency can be written as the product of a term describing the vector additions and a term containing physical properties and constants:

$$\Omega(F, m_F, F', m'_F, q) = C(F, m_F, F', m'_F, I, S, L, L', J, J', q)\sqrt{\frac{3\lambda^3\Gamma I}{4\pi^2 c\hbar}} \tag{34}$$

where the coefficient is given by

$$\begin{aligned} C(F, m_F, F', m'_F, I, S, L, L', J, J', q) &= (-1)^{\frac{1}{2}q(1+q)+1+2F-m_F+I+J'+S+L'+J} \\ &\times \sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)(2L+1)} \\ &\times \begin{pmatrix} F & 1 & F' \\ -m_F & q & m'_F \end{pmatrix} \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix} \begin{Bmatrix} L & J & S \\ J' & L' & 1 \end{Bmatrix}. \end{aligned} \tag{35}$$

We consider the calculation of the Rabi Frequency for the hyperfine transition $n^2S_{1/2}(F = 2, m_F = 2)$–$n'^2P_{3/2}(F = 2, m_F = 2)$, which would exist in a single-valence-electron atom such as an alkali. The $3j$ and $6j$ symbols of equation (17) can be evaluated from the tables found in standard texts [7, 8] or directly from some computer algebra software packages [12, 13]. For this transition, equation (17) yields

$$\Omega(2, 2, 2, 2, 0) = -\sqrt{3}\sqrt{\frac{3\lambda^2\Gamma I}{4\pi^2 c\hbar}}. \tag{36}$$

Using the standard angular momentum coupling formula, the calculation proceeds as follows. First, equation (8) produces

$$\langle 22|D_q|22\rangle^F = \frac{1}{\sqrt{2}}\langle \tfrac{3}{2}\tfrac{1}{2}|D_q|\tfrac{1}{2}\tfrac{1}{2}\rangle^J \tag{37}$$

where the superscript on the matrix elements defines the representation. For the evaluation in this case, equation (8) consists of one term only since the requirement of $\delta(m_I, m'_I)$ imposes the condition

$$m_I = 2 - m_J = 2 - m'_J \tag{38}$$

which results in the only permitted values for m_J and m'_J being $\frac{1}{2}$. Next, the matrix element in the J representation is evaluated by equation (9)

$$\langle \tfrac{3}{2}\tfrac{1}{2}|D_q|\tfrac{1}{2}\tfrac{1}{2}\rangle^J = \sqrt{\frac{2}{3}}\langle 10|D_q|00\rangle^L. \tag{39}$$

Application of the Wigner–Eckart theorem, equation (10), then removes the m_I dependence, giving

$$\langle 10|D_q|00\rangle^L = \frac{1}{\sqrt{3}}\langle 1||D||0\rangle^L. \tag{40}$$

The reduced matrix element is evaluated from equation (11)

$$\langle 1||D||0\rangle^L = \sqrt{3}\left(\frac{3\varepsilon_0\hbar\lambda^3\Gamma}{8\pi^2}\right)^{1/2}. \tag{41}$$

Sequential substitution of equations (41), (40) and (39) into equation (37), followed by substitution of the result into equation (5), yields equation (36) again.

Finally, equation (36) can be obtained from the procedures of Condon and Shortley for evaluating the matrix element. Applying the appropriate equation from the set 9^311 of Condon and Shortley, for the particular example considered here, yields

$$\langle 22|D|22\rangle^F = \langle 2\dot{:}D\dot{:}2\rangle^F 2k. \tag{42}$$

The Condon and Shortley reduced matrix element in the F representation can be expressed in terms of a reduced matrix element in the J representation employing the appropriate equation from 11^38 which is

$$\langle J_1J_2J\dot{:}D\dot{:}J_1J_2-1J\rangle = \{\pm\}\langle J_1J_2\dot{:}D\dot{:}J_1J_2-1\rangle\frac{\sqrt{P(J)Q(J)}}{2J(J+1)} \tag{43}$$

where

$$P(J) = (J-J_1+J_2)(J+J_1+J_2+1) \tag{44a}$$

$$Q(J) = (J_1+J_2-J)(J+J_1-J_2+1). \tag{44b}$$

The right-hand side is expressed with an alternate sign which is governed by the choice of the phases of the states. To be consistent with the previous two methods of calculation, the upper alternative is chosen wherever there is an option available. Taking $J_1 = I$, $J_2 = L$, $J = F$ and substituting values appropriate to the example results in

$$\langle \tfrac{3}{2}\tfrac{3}{2}2\dot{:}D\dot{:}\tfrac{3}{2}\tfrac{1}{2}2\rangle^F = \tfrac{1}{2}\langle \tfrac{3}{2}\tfrac{3}{2}\dot{:}D\dot{:}\tfrac{3}{2}\tfrac{1}{2}\rangle^J. \tag{45}$$

The element in the J representation is further reduced to the L representation using the following equation 11^38 from Condon and Shortley:

$$\langle J_1J_2J\dot{:}D\dot{:}J_1J_2-1J-1\rangle = \langle J_1J_2\dot{:}D\dot{:}J_1J_2-1\rangle\frac{\sqrt{P(J)P(J-1)}}{2J\sqrt{(2J-1)(2J+1)}} \tag{46}$$

to give, with $J_1 = S$, $J_2 = L$ and $J = J$,

$$\langle \tfrac{1}{2}1\tfrac{3}{2}\dot{:}D\dot{:}\tfrac{1}{2}0\tfrac{1}{2}\rangle^J = \frac{1}{\sqrt{3}}\langle \tfrac{1}{2}1\dot{:}D\dot{:}\tfrac{1}{2}0\rangle^L. \tag{47}$$

Combining equations (42), (45) and (47), the matrix element in the F representation can now be expressed in terms of the Condon and Shortley reduced matrix element in the L representation

$$\langle 22|D|22\rangle^F = \frac{1}{\sqrt{3}}\langle 1\dot{:}D\dot{:}0\rangle^L k \tag{48}$$

where the S quantum number has been omitted in the L representation element. A Condon and Shortley reduced matrix element of the form $\langle J\dot{:}T\dot{:}J-1\rangle$ is related to the standard reduced matrix element by [7]

$$\langle J||D||J-1\rangle = \sqrt{J(2J-1)(2J+1)}\langle J\dot{:}D\dot{:}J-1\rangle. \tag{49}$$

In terms of the standard reduced matrix element, equation (46) then becomes

$$\langle 22|D|22\rangle^F = \tfrac{1}{3}\langle 1||D||0\rangle^L k. \tag{50}$$

For comparison with the other two methods, the Cartesian coordinates of the Condon and Shortley terms must be transformed to the spherical basis set using equation (2). Then, evaluating the reduced matrix element from equation (11) and substituting into equation (5) for the Rabi frequency, the result of equation (36) is once again produced.

Values of the coefficient $C(F, m_F, F', m'_F, I, S, L, L', J, J', q)$ for an $n^2S_{1/2}$–$n'^2P_{3/2}$ manifold of transitions are given in table 1.

Table 1. Values of the Rabi frequency coefficient $C(F, m_F, F', m'_F, I, S, L, L', J, J', q)$ for an $n^2S_{1/2}$–$n'^2P_{3/2}$ manifold of transitions.

		m_F				
q	F	−2	−1	0	1	2
$n^2S_{1/2}(F=1)$–$n'^2P_{3/2}(F)$						
1	0		$1/\sqrt{3}$			
1	1		$-5/\sqrt{60}$	$-5/\sqrt{60}$		
1	2		$1/\sqrt{12}$	$1/2$	$1/\sqrt{2}$	
0	0			$1/\sqrt{3}$		
0	1		$5/\sqrt{60}$	0	$-5/\sqrt{60}$	
0	2		$-1/2$	$-1/\sqrt{3}$	$-1/2$	
−1	0				$-1/\sqrt{3}$	
−1	1			$-5/\sqrt{60}$	$-5/\sqrt{60}$	
−1	2		$-1/\sqrt{2}$	$-1/2$	$-1/\sqrt{12}$	
$n^2S_{1/2}(F=2)$–$n'^2P_{3/2}(F)$						
1	1	$1/\sqrt{10}$	$1/\sqrt{20}$	$1/\sqrt{60}$		
1	2	$-1/\sqrt{6}$	$-1/2$	$-1/2$	$-1/\sqrt{6}$	
1	3	$1/\sqrt{15}$	$1/\sqrt{5}$	$2/\sqrt{10}$	$2/\sqrt{6}$	1
0	1		$1/\sqrt{20}$	$1/\sqrt{15}$	$1/\sqrt{20}$	
0	2	$1/\sqrt{3}$	$1/\sqrt{12}$	0	$-1/\sqrt{12}$	$-1/\sqrt{3}$
0	3	$-1/\sqrt{3}$	$-4/\sqrt{30}$	$-3/\sqrt{15}$	$-4/\sqrt{30}$	$-1/\sqrt{3}$
−1	1			$-1/\sqrt{60}$	$-1/\sqrt{20}$	$-1/\sqrt{10}$
−1	2		$-1/\sqrt{6}$	$-1/2$	$-1/2$	$-1/\sqrt{6}$
−1	3	−1	$-2/\sqrt{6}$	$-2/\sqrt{10}$	$-1/\sqrt{5}$	$-1/\sqrt{15}$

In the calculation of the dipole matrix element by any of the three methods, the ordering of the quantum numbers in a state expansion is of crucial importance in obtaining consistency in the sign. In each case, we have maintained the convention of writing the element as $\langle J_1 J_2 J m_J|D|J_1 J'_2 J' m'_J\rangle$, where D commutes with J_1, which, in these calculations, is either

I or S. A different convention would be required if the matrix element was written such that D commuted with J_2. For example, in equation (43), the opposite sign is chosen to that of the convention chosen for when D commutes with J_1. Since all other signs remain unchanged, the net effect of rewriting the matrix element would be to invert the sign of the Rabi frequency for the $n^2S_{1/2}(F=2, m_F=2)$–$n'^2P_{3/2}(F=2, m_F=2)$ transition. For the standard angular momentum coupling formula method, the assumption that D commutes with J_2 amounts to reordering the J_1 and J_2 quantum numbers in the Clebsch–Gordan coefficients and, hence, the $3j$ symbols. Using the relationship for $3j$ symbols that

$$\begin{pmatrix} J_2 & J_1 & J \\ m_2 & m_1 & -m \end{pmatrix} = (-1)^{J_1+J_2+J} \begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & -m \end{pmatrix} \tag{51}$$

equations (8) and (9) produce a change in sign for this transition. With respect to the reduction formula for composite systems method, an alternate form of equation (13) is required if the operator commutes with J_2, namely

$$\langle J_1 J_2 J || U^k || J_1' J_2 J' \rangle = (-1)^{J_1+J_2+J'+k} \langle J_1 || U^k || J_1' \rangle \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J_1 & J & J_2 \\ J' & J_1' & k \end{Bmatrix}. \tag{52}$$

Evaluating the reduced matrix elements of equations (15) and (16), with the ordering of I and J and S and L reversed to accommodate the altered commutation convention, once again changes the sign of the Rabi frequency. Hence, changing the ordering convention reverses the sign of the Rabi frequency for the particular transition considered here, however, the three methods remain consistent. The values of the Rabi-frequency coefficient, calculated for the $n^2S_{1/2}$–$n'^2P_{3/2}$ transition under the altered convention display, changed signs for all transitions for which ΔF was equal to zero. Observable quantities calculated using the amended table of values will be identical to those using table 1 since the phase of the individual Rabi frequency cannot be detected. However, if the observable was the result of more than one process, care would be required to be consistent in the choice of the ordering convention.

5. Conclusion

Three different methods of calculating the dipole matrix elements necessary for the evaluation of Rabi frequencies have been summarized. Contrary to previous work, we have shown that each of the methods produces the identical result as long as care is taken to be consistent in the convention used in ordering the quantum numbers in the matrix elements. Without doubt, the most convenient method is to apply the reduction formula for composite systems, since this is the only method that results in a single term expression of the form of equation (17) for the Rabi frequency.

The need to evaluate matrix elements arises in other applications; for example, in expressing a density matrix element in hyperfine representation in terms of its element in the L representation. Since there is no tensor operator involved, the only method suitable is that using the standard angular momentum coupling formula. Alternatively, if the complete vector property of a matrix element is required, when calculating fluorescence intensity with the detection operator $\sum_m f \cdot D|m\rangle\langle m|f^* \cdot D$ for example, the method of Condon and Shortley is the most appropriate.

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