

# The relationship between perturbation theory and direct calculations of rare earth transition intensities

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## Abstract

We use a simplified calculation to demonstrate the equivalence between three different methods for calculating transition line strengths. These calculations demonstrate the complex interplay between spin-orbit and correlation contributions to two-photon transitions in rare earth ions.

## 1. Introduction

In a previous paper we investigated many-body perturbation theory calculations of two-photon transition intensities in  $Gd^{3+}$  [1]. We found incompatibilities between the many-body formalism and the earlier calculations of Judd and Pooler [2] and Downer and co-workers [3] because the latter contain “unlinked” diagrams. Removal of these diagrams seemed to destroy the previous good agreement between theory and experiment. Agreement was restored, however, when “folded” third-order correlation diagrams involving the Coulomb interaction within the  $4f^7$  configuration were included. The question that remained unanswered was how these two apparently incompatible calculations could yield similar answers.

More recently, we performed “direct” calculations for  $Eu^{2+}$ , in which the actual eigenstates of the  $4f^7$  and  $4f^65d$  configurations were used [4]. That work clarified the interplay between Coulomb and spin-orbit contributions to two-photon transition intensities and provided a way to reconcile the different methods of calculation.

It is the purpose of this paper to explicitly demonstrate this reconciliation. A key point is that the “folded” diagrams represent changes in energy from the configuration average. Thus, if we are only interested in

a restricted range of energy levels, we can use the “true” energies instead, in which case the Judd–Pooler calculations give correct results. To show this, we briefly review the Rayleigh–Schrödinger perturbation theory. We then consider a simplified four-state system, showing the equivalences between direct, many-body perturbation, and Judd–Pooler type perturbation calculations.

## 2. Perturbation theory

The many-body perturbation theory approach used in ref. 1 is developed in detail in Chapters 9 and 13 of the book by Lindgren and Morrison [5]. When the formalism is extended to include atom–photon interactions, the energy denominators are modified by the inclusion of photon energies [6], but the same diagrams occur. The calculations employ the concept of a “model space”. Rather than solving for the eigenvalues and eigenstates of the full Hamiltonian, an “effective Hamiltonian” is constructed and diagonalized within the model space, and the expectation values of “effective transition operators” are evaluated between the model-space eigenvectors.

Initially, we use Rayleigh–Schrödinger perturbation theory on the level of Chapter 9 of Lindgren and Morrison. If we only consider excited configurations of opposite parity to the ground configuration, the relevant second- and third-order equations for the two-photon absorption transition moments are

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$$\sum_S \frac{\langle K|\mathbf{r}|S\rangle\langle S|\mathbf{r}|I\rangle}{(E_I - E_S + \omega)} \quad (1)$$

$$\sum_{ST} \frac{\langle K|\mathbf{r}|T\rangle\langle T|V|S\rangle\langle S|\mathbf{r}|I\rangle}{(E_I - E_T + \omega)(E_I - E_S + \omega)} \quad (2)$$

$$- \sum_{JS} \frac{\langle K|\mathbf{r}|S\rangle\langle S|\mathbf{r}|J\rangle\langle J|V|I\rangle}{(E_J - E_S + \omega)(E_I - E_S + \omega)} \quad (3)$$

In these expressions,  $I$ ,  $J$  and  $K$  are states within the model space ( $4f^N$ ) and  $S$  and  $T$  are states in an excited configuration (e.g.  $4f^{N-1}5d$ ) outside the model space. The perturbation,  $V$ , includes the spin-orbit and Coulomb interactions,  $\mathbf{r}$  is the dipole moment operator, and  $\omega$  is the photon energy ( $\hbar=1$ ). If desired, eqn. (3), may be Hermitized by averaging with its conjugate. However, it should be noted that model-space calculations are inherently non-Hermitian.

When excited configurations having the same parity as the ground configuration are included, we have the two additional equations,

$$\sum_{MS} \frac{\langle K|\mathbf{r}|S\rangle\langle S|\mathbf{r}|M\rangle\langle M|V|I\rangle}{(E_I - E_S + \omega)(E_I - E_M)} \quad (4)$$

$$\sum_{SM} \frac{\langle K|V|M\rangle\langle M|\mathbf{r}|S\rangle\langle S|\mathbf{r}|I\rangle}{(E_I - E_M + 2\omega)(E_I - E_S + \omega)} \quad (5)$$

where the  $M$  are states in an excited configuration of the same parity as the ground configuration (e.g.  $4f^{N-1}5f$ ). For the simplified calculations that follow, however, only a single excited configuration will be considered, and thus contributions from eqns. (4), (5) will not arise.

The above equations will be used for each of the three calculations that follow. The fundamental differences between these calculations are not in the equations used, but rather in their differing definitions of the states  $|i\rangle$  and energies  $E_i$ . For the direct calculation, eigenstates and eigenvalues of the complete Hamiltonian will be used, allowing only contributions from eqn. (1). In contrast, the many-body calculation uses zero-order eigenstates, necessitating the use of all relevant equations. The Judd–Pooler type perturbation calculation uses the zero-order eigenstates within the excited configuration (like the many-body calculation) and uses exact eigenstates within the ground configuration (like the direct calculation). Thus, Judd–Pooler type calculations omit eqn. (3), which has the perturbation  $V$  acting within the ground configuration. In the next section, we show that when careful attention is paid to these differences, all three calculations result in equivalent answers.

### 3. Simplified calculation

We consider a simplified system with four states,  $|a\rangle$ ,  $|b\rangle$ ,  $|c\rangle$  and  $|d\rangle$ . The model space consists of  $|a\rangle$  and  $|b\rangle$ , while  $|c\rangle$  and  $|d\rangle$  are excited states. The Hamiltonian,  $H$ , is divided into a zero-order part,  $H_0$ , and a perturbation,  $V$ ,

$$H = H_0 + V = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \Delta & 0 \\ 0 & 0 & 0 & \Delta \end{bmatrix} + \begin{bmatrix} C_a & Z_1 & 0 & 0 \\ Z_1 & C_b & 0 & 0 \\ 0 & 0 & C_c & Z_2 \\ 0 & 0 & Z_2 & C_d \end{bmatrix} \quad (6)$$

where  $\Delta$  is the zero-order energy difference between the excited and model spaces (the Hartree–Fock energy). The  $C_i$  represent the non-spherical part of the Coulomb interaction, and the  $Z_j$  represent the spin-orbit interaction. The effective Hamiltonian for the model space is

$$H_{\text{eff}} = \begin{bmatrix} C_a & Z_1 \\ Z_1 & C_b \end{bmatrix} \quad (7)$$

In the general case, there could be matrix elements of  $V$  (e.g. the odd-parity crystal field) connecting  $|a\rangle$  and  $|b\rangle$  to  $|c\rangle$  and  $|d\rangle$ . In that case, eqn. (7) would be a first-order approximation to  $H_{\text{eff}}$ .

If the  $Z_j$  are small compared to the  $C_i$ , we can take the mixing to first order in the  $Z_j$  and ignore the energy shift. This yields the following expressions for the  $|i'\rangle$  eigenstates of  $H$ :

$$|a'\rangle = |a\rangle + |b\rangle \frac{Z_1}{C_a - C_b}, \quad E_{a'} = C_a \quad (8)$$

$$|b'\rangle = |b\rangle + |a\rangle \frac{Z_1}{C_b - C_a}, \quad E_{b'} = C_b \quad (9)$$

$$|c'\rangle = |c\rangle + |d\rangle \frac{Z_2}{C_c - C_d}, \quad E_{c'} = \Delta + C_c \quad (10)$$

$$|d'\rangle = |d\rangle + |c\rangle \frac{Z_2}{C_d - C_c}, \quad E_{d'} = \Delta + C_d \quad (11)$$

The states  $|a'\rangle$  and  $|b'\rangle$  are also the eigenstates of  $H_{\text{eff}}$ .

We take the one-photon interaction matrix to be

$$M = \begin{bmatrix} 0 & 0 & T_1 & 0 \\ 0 & 0 & 0 & T_2 \\ T_1 & 0 & 0 & 0 \\ 0 & T_2 & 0 & 0 \end{bmatrix} \quad (12)$$

where the  $T_k$  represent dipole moments. Two-photon transitions between  $|a'\rangle$  and  $|b'\rangle$  are “spin-forbidden”, as they are allowed only due to the presence of the “spin-orbit” matrix elements,  $Z_j$ , in the Hamiltonian.

### 3.1. Direct calculation

In order to perform an “exact” or “direct” calculation of the two-photon transition moment for the “spin-forbidden”  $|a'\rangle$  to  $|b'\rangle$  transition, we use exact eigenstates of  $H$ , rather than those of  $H_0$ . This makes the third-order terms superfluous, and only the second-order matrix elements of eqn. (1) must be evaluated.

Rather than write out all possible terms, we present only those that are quadratic in  $T_2$  and linear in  $Z_1$ . From eqn. (1), we obtain

$$\left(\frac{T_2 T_2}{C_a - (\Delta + C_d) + \omega}\right) \left(\frac{Z_1}{C_a - C_b}\right) \quad (13)$$

where the first fraction represents the second-order time dependent perturbation, and the second fraction gives the proportion of  $|b\rangle$  in  $|a'\rangle$ . Expanding eqn. (13) in powers of  $1/(-\Delta + \omega)$ , we obtain

$$\frac{T_2 T_2 Z_1}{C_a - C_b} \left( \frac{1}{-\Delta + \omega} + \frac{C_d - C_a}{(-\Delta + \omega)^2} + \dots \right) \quad (14)$$

### 3.2. Many-body perturbation calculation

The states in eqns. (1)–(3) represent configurational states, whereas many-body perturbation theory is expressed in terms of orbitals. However, the correspondence between eqns. (1)–(3) and orbital expressions is exact (see Chapter 13 of refs. 5 and 7), and for the purposes of this discussion, we use eqns. (1)–(3) to demonstrate the results of a many-body calculation. Our calculation is based on Rayleigh–Schrödinger perturbation theory, so eigenvalues of  $H_0$  are used in the energy denominators. Furthermore, the states in eqns. (1)–(3) are the zero-order states ( $|i\rangle$ , not  $|i'\rangle$ ). In order to obtain the terms containing  $T_2 T_2 Z_1$ , we place these “effective transition operators” between the eigenstates of  $H_{\text{eff}}$ . This leads to the factors  $Z_1/(C_a - C_b)$  in some of the following expressions. From eqn. (1), we obtain

$$\frac{T_2 T_2}{-\Delta + \omega} \left(\frac{Z_1}{C_a - C_b}\right) \quad (15)$$

Restricting  $V$  to the spin-orbit interaction in eqn. (2), we only obtain terms involving  $Z_2$ . However, letting  $V$  contain the Coulomb interaction yields

$$\frac{T_2 C_d T_2}{(-\Delta + \omega)(-\Delta + \omega)} \left(\frac{Z_1}{C_a - C_b}\right) \quad (16)$$

Equation (3) yields

$$-\frac{T_2 T_2 Z_1}{(-\Delta + \omega)(-\Delta + \omega)} \\ = -\frac{T_2 T_2 Z_1}{(-\Delta + \omega)(-\Delta + \omega)} \times \left(\frac{C_a - C_b}{C_a - C_b}\right) \quad (17)$$

$$\text{and } -\frac{T_2 T_2 C_b}{(-\Delta + \omega)(-\Delta + \omega)} \left(\frac{Z_1}{C_a - C_b}\right) \quad (18)$$

from the spin-orbit and Coulomb contributions, respectively. Adding these terms together, we obtain

$$\frac{T_2 T_2 Z_1}{C_a - C_b} \left( \frac{1}{-\Delta + \omega} + \frac{C_d - (C_a - C_b) - C_b}{(-\Delta + \omega)^2} \right) \quad (19)$$

which is the same as the “direct” calculation. Note the cancellation between eqns. (17) and (18), which arise from “spin-orbit” and “Coulomb” interactions, respectively.

### 3.3. Judd–Pooler perturbation calculation

The original Judd–Pooler [2] calculation does not include eqn. (3) and thus eqns. (17),(18) do not arise. However, the denominators now contain eigenvalues of  $H_{\text{eff}}$  and eqn. (1) yields

$$\left(\frac{T_2 T_2}{C_a - \Delta + \omega}\right) \left(\frac{Z_1}{C_a - C_b}\right) \quad (20)$$

Coulomb contributions within the excited configuration were considered to be small in the calculations of Judd and Pooler, and were therefore neglected. For completeness, however, we include them here. Thus, from eqn. (2), we obtain

$$\left(\frac{T_2 C_d T_2}{(C_a - \Delta + \omega)(C_a - \Delta + \omega)}\right) \left(\frac{Z_1}{C_a - C_b}\right) \quad (21)$$

Adding these terms together and expanding in powers of  $1/(-\Delta + \omega)$ , we obtain

$$\frac{T_2 T_2 Z_1}{C_a - C_b} \left( \frac{1}{-\Delta + \omega} + \frac{C_d - C_a}{(-\Delta + \omega)^2} + \dots \right) \quad (22)$$

which is the same as the results of the direct calculation (eqn. (14)) and the many-body perturbation calculation (eqn. (19)). We have emphasized terms containing  $T_2 T_2 Z_1$ , in order to display expressions arising from eqn. (3). In general, when terms involving any combination of matrix elements are evaluated, with perturbation expansions carried out to  $n$ th order, agreement is exact through the  $n-1$  order of  $1/(-\Delta + \omega)$ . Thus, to achieve agreement between these three calculations in the third order of  $1/(-\Delta + \omega)$ , it would be necessary to consider fourth-order perturbation terms.

In essence, as explained in ref. [4], the Judd–Pooler calculation has moved the part of  $V$  that acts within the model space into  $H_0$ . This means that the matrix element  $\langle J|V|I \rangle$  of eqn. (3) is equal to zero, since there is no longer any  $V$  separate from  $H_0$  acting within the model space. The Judd–Pooler calculation is therefore correct, but it must be realized that different energy

denominators should be used for transitions between different energy levels.

In Judd–Pooler-type calculations (eqn. (20)), terms containing the Coulomb matrix elements,  $C_i$ , arise from using eigenvalues of  $H_{\text{eff}}$ , which includes effects of the Coulomb interaction. In many-body perturbation calculations, by contrast, they arise only from perturbation expressions containing the Coulomb interaction explicitly. Therefore, the classification of contributions as “spin-orbit” or “correlation” depends, in part, upon the method of calculation.

#### 4. Many-body perturbation theory for $\text{Gd}^{3+}$

For the  $\text{Gd}^{3+}$  calculation discussed in ref. 1, the states in eqns. (1)–(5) represent states in the  $4f^7$  and  $4f^65d$  configurations. Many-body perturbation theory, however, is expressed in terms of *orbitals*. The transformation from eqns. (1)–(5) to expressions corresponding to the diagrams evaluated in ref. 1 is explained by Lindgren and Morrison [5, Chapter 13]; see also [7].

Ignoring diagrams involving core excitations, we have only one second-order diagram and four third-order diagrams involving the spin-orbit interaction,  $V_{\text{so}}$ , and the dipole moment,  $\mathbf{r}$ . These are shown in Fig. 1(a–f), and have corresponding algebraic expressions

$$a_k^\dagger a_i \sum_s \frac{\langle k|\mathbf{r}|s\rangle\langle s|\mathbf{r}|i\rangle}{\epsilon_i - \epsilon_s + \omega} \quad (23)$$

$$a_k^\dagger a_i \sum_{st} \frac{\langle k|\mathbf{r}|t\rangle\langle t|V_{\text{so}}|s\rangle\langle s|\mathbf{r}|i\rangle}{(\epsilon_i - \epsilon_t + \omega)(\epsilon_i - \epsilon_s + \omega)} \quad (24)$$

$$-a_k^\dagger a_i \sum_{js} \frac{\langle k|\mathbf{r}|s\rangle\langle s|\mathbf{r}|j\rangle\langle j|V_{\text{so}}|i\rangle}{(\epsilon_i - \epsilon_s + \omega)(\epsilon_j - \epsilon_s + \omega)} \quad (25)$$

$$a_k^\dagger a_i \sum_{ms} \frac{\langle k|\mathbf{r}|s\rangle\langle s|\mathbf{r}|m\rangle\langle m|V_{\text{so}}|i\rangle}{(\epsilon_i - \epsilon_s + \omega)(\epsilon_i - \epsilon_m)} \quad (26)$$

$$a_k^\dagger a_i \sum_{ms} \frac{\langle k|V_{\text{so}}|m\rangle\langle m|\mathbf{r}|s\rangle\langle s|\mathbf{r}|i\rangle}{(\epsilon_i - \epsilon_m + 2\omega)(\epsilon_i - \epsilon_s + \omega)} \quad (27)$$

In these expressions,  $i, j$  and  $k$  label valence ( $4f$ ) orbitals in our  $4f^7$  model space,  $s$  and  $t$  label virtual orbitals outside the model space ( $5d$ ), and the  $\epsilon$  are orbital energies. Each term contains a product of a creation operator and an annihilation operator for  $4f$  orbitals. The diagram corresponding to eqn. (25) (Fig. 1(c)) is commonly referred to as “folded” [5].

Equation (23) arises directly from eqn. (1). Equation (24) arises from eqn. (2), where the spin-orbit interaction and the dipole moments act on the same electron. “Unlinked” expressions (Fig. 1(d)), where the dipole moments and the spin-orbit operator act on different electrons, arise from both eqn. (2) and eqn. (3) and

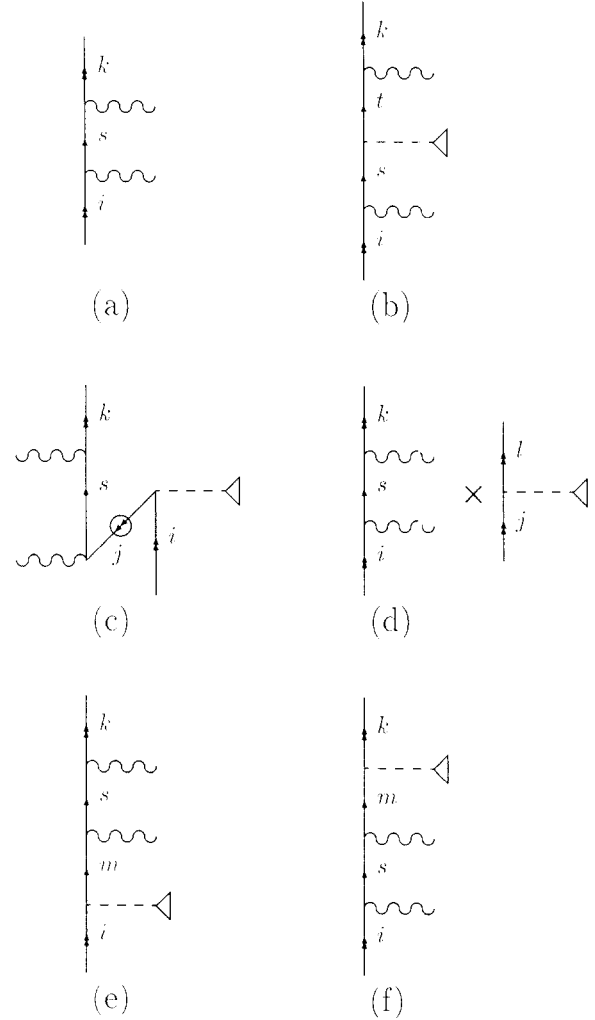


Fig. 1. Second and third-order one-electron two-photon absorption diagrams. For details of notation see ref. [5]. A single up-going arrow represents a virtual orbital, a double arrow a valence orbital. Folded valence lines have a circle around their arrows. Photons are represented by wavy lines and the spin-orbit interaction by a triangle. Diagrams (a), (b), (c), (e) and (f) correspond to eqns. (23)–(27) of the text, respectively. Diagram (c) is folded, diagram (d) is unlinked.

cancel. This leaves us with the “folded” diagram (Fig. 1(c), eqn. (25)) which arises from eqn. (3) when the dipole moments and spin-orbit operator act on the same electron.

It is important not to confuse “folded” diagrams with “core excitations”. The folding is merely a device to preserve the rules for calculating the denominators [5] (especially pp. 304–305). In Fig. 1(c), for example, an electron is excited from state  $i$  to  $j$  to  $s$  to  $k$ , and the diagram does not imply that there is initially an electron in state  $j$ , as is clear from the operator ordering of eqn.(25).

Equations (26) and (27) arise from eqns. (4) and (5). These have been overlooked in earlier work [1–3]. Their possible importance has been recently demonstrated by Smentek-Mielczarek [8].

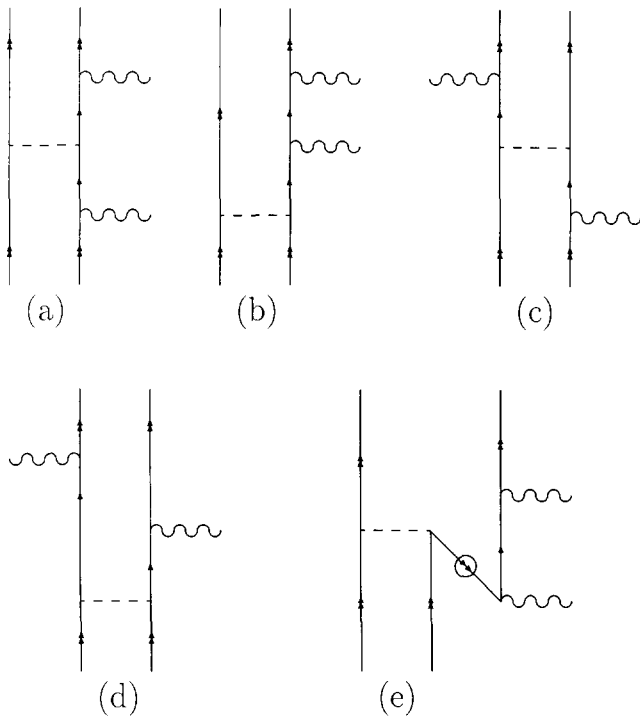


Fig. 2. Some third-order two-electron two-photon absorption diagrams. Notation is the same as Fig. 1. The Coulomb interaction is represented by a dotted line. Folded diagram (e) dominates the correlation calculation of ref. [1].

Some third-order “correlation” diagrams involving the Coulomb interaction are shown in Fig. 2. The folded diagram, Fig. 2(e), arises from eqn. (3), when  $V$  is the Coulomb interaction. It gives a large contribution in the calculations of ref. 1, since it represents perturbations to the energy-levels of the  $f^7$  configuration caused by the Coulomb interaction. An analogous term in our simplified calculation is eqn. (18). As in our simplified calculation, it is possible to take these effects into account implicitly by using the exact energy levels. Thus, the agreement between the calculation of ref. 1 and the calculation of Judd and Pooler [2] (in which the correlation effects are absorbed into the denominators) is not merely fortuitous, but is a result of doing the same calculation in different ways.

## 5. Conclusion

Careful application of three different calculation methods (direct [4], many-body perturbation [1], and

Judd–Pooler [2,3] type perturbation calculations) yields identical results. Thus, each of these three methods may legitimately be used in the calculation of transition line strengths.

The Judd–Pooler [2] calculation, while valid, is not compatible with Lindgren and Morrison’s [5] formulation of many-body perturbation theory. This is because the Judd–Pooler zero-order Hamiltonian,  $H_0$ , is different when acting upon ground configuration states than when acting upon states of the excited configuration, thus destroying the cancellation of unlinked diagrams necessary for the many-body perturbation theory. In contrast, the direct calculations used in ref. [4] and illustrated here are compatible with MBPT, as long as we define the model space to include both the  $4f^N$  and the  $4f^{N-1}5d$  configurations. In that case, it is possible to add contributions from other excited configurations or from other potential terms, using the techniques of MBPT. In fact, we feel that this will be a most profitable direction for future calculations, particularly for examination of transition intensities for divalent lanthanides, where both the Judd–Pooler formalism [3] and the more straightforward MBPT calculations, using  $4f^N$  as the model space, have been shown to be insufficient [4].

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