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LETTER TO THE EDITOR

Correlation contributions to two-photon lanthanide absorption intensities: direct calculations for Eu^{2+} ions

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Abstract. We calculate two-photon intensities for $^8\text{S}_{7/2} \rightarrow ^6\text{P}_J, ^6\text{D}_J$ transitions in Eu^{2+} -doped CaF_2 using eigenstates of the Coulomb and spin-orbit interactions within both the ground $4f^7$ and excited $4f^65d$ configurations. Good agreement with experiment is achieved. In particular, we explain observed $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ transition intensities, which previous calculations had overestimated by a factor of more than 100. We also examine the relationship between the direct calculations presented here and various perturbation methods.

In the early 1980s, Downer [1] performed extensive two-photon transition intensity measurements within the $4f^7$ configuration of Gd^{3+} ions doped into LaF_3 and in aqueous solution. Downer and Bivas [2] were able to explain observed $^8\text{S}_{7/2} \rightarrow ^6\text{P}_J, ^6\text{D}_J$ transition intensities using extensions to the second-order theory of Axe [3] that include third-order contributions involving spin-orbit interactions within the $4f^65d$ excited configuration [4]. Upon the inclusion of third- and fourth-order contributions involving excited-configuration crystal-field interactions, they were able to explain the remaining $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ transitions, which break the $\Delta L \leq 2, \Delta J \leq 2$ selection rules.

However, the theory was much less successful in explaining transitions in the isoelectronic Eu^{2+} ion doped in CaF_2 [5]. At that time, Downer *et al* [5] suggested that correlation contributions might account for the large discrepancies between calculations and experiment. Although they performed some qualitative calculations in their feasibility argument, neither they nor subsequent researchers performed the necessary quantitative calculations. Later calculations by Smentek-Mielczarek and Hess [6] illustrated the importance of correlation, but since the terms calculated simply provide an overall scaling, they do not affect theoretical fittings to experiment.

We recently presented [7] a re-analysis of the spin-orbit extensions of Judd and Pooler [4] for $^8\text{S}_{7/2} \rightarrow ^6\text{P}_J$ transitions of Gd^{3+} , in which we also evaluated correlation contributions. In that analysis, we discovered that a large portion of the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ transition intensity, previously attributed to spin-orbit contributions, appears to come from neglected correlation contributions within the ground configuration. Motivated by this demonstrated importance of correlation in Gd^{3+} transitions, it is the purpose of this letter to show that inclusion of correlation contributions can explain observed absorption intensities for the isoelectronic Eu^{2+} ion. We also discuss the relationship between direct calculations presented here and the differing perturbation methods used in [4] and [7].

In our correlation calculations for Gd^{3+} [7], we found that the radial integrals $R^k(4f4f, 4f4f)$ were of the same order or magnitude as the energy difference between the $4f^7$ and

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4f⁶5d configurations. Thus, in order to achieve convergence, it was necessary to consider higher orders of the perturbation expansions containing these radial integrals. Since the 4f⁶5d configuration lies at a much lower energy for Eu²⁺ than for Gd³⁺, this problem is even more pronounced in Eu²⁺, causing the perturbation expansions to diverge. Thus, it seems preferable to use direct calculation [8, 9] rather than perturbation theory to calculate correlation contributions to transition intensities in the divalent Eu²⁺ ion.

Instead of using the closure approximation and invoking higher-order corrections, we can directly calculate two-phonon effective matrix elements from the second-order equation

$$M_{fi} = \sum_{\nu} \frac{\langle f | \epsilon \cdot D | \nu \rangle \langle \nu | \epsilon \cdot D | i \rangle}{E_i - E_{\nu} + \hbar\omega} \quad (1)$$

where ϵ is the polarization vector of the radiation, $\hbar\omega$ is the single-photon energy, and i , f , and ν are eigenstates of the complete Hamiltonian. That is, Coulomb and spin-orbit effects are incorporated into the diagonalization of the excited-configuration wavefunctions $|\nu\rangle$, as well as the ground-configuration wavefunctions $|i\rangle$ and $|f\rangle$. The summation is taken over all states within the excited configuration, with exact energy denominators calculated for each ν .

It is not practical to use individual Stark components in our calculation, since they are so numerous. Considering Stark components for each multiplet to be degenerate, we can apply the Wigner-Eckart theorem to (1). We then decouple the radiation polarization from the electric dipole operators to obtain

$$M_{E'J'-EJ} = \sum_k (-1)^{k+J'+J} \sqrt{2k+1} \{\epsilon\epsilon\}^{(k)} \sum_{E''J''} \begin{Bmatrix} 1 & k & 1 \\ J' & J'' & J \end{Bmatrix} \\ \times \frac{\langle E'J' || D^{(1)} || E''J'' \rangle \langle E''J'' || D^{(1)} || EJ \rangle}{E - E'' + \hbar\omega} \quad (2)$$

where each eigenstate is labelled by its eigenvalue E and total momentum J . The polarization dependence is completely contained in $\{\epsilon\epsilon\}^{(k)}$. Absolute line strengths for each transition are proportional to the squares of these effective matrix elements. Note that in the squaring process, cross-terms between different k cancel out for total multiplet-multiplet intensities.

It is useful to consider the relationship between the direct calculation of (2) and the different perturbation theory expressions used in [4] and [7]. This can help us understand why the Gd³⁺ calculations of Judd and Pooler [4] and Burdick and Reid [7] are apparently so different, yet give almost the same answer.

To third order, the perturbation expansion is

$$M_{fi} = \sum_{\nu} \frac{\langle f | \epsilon \cdot D | \nu \rangle \langle \nu | \epsilon \cdot D | i \rangle}{E_i - E_{\nu} + \hbar\omega} \\ + \sum_{\nu u} \frac{\langle f | \epsilon \cdot D | \nu \rangle \langle \nu | V | u \rangle \langle u | \epsilon \cdot D | i \rangle}{(E_i - E_{\nu} + \hbar\omega)(E_i - E_u + \hbar\omega)}$$

$$\begin{aligned}
 & -\frac{1}{2} \left[\sum_{vf'} \frac{\langle f|V|f'\rangle \langle f'|\epsilon \cdot D|v\rangle \langle v|\epsilon \cdot D|i\rangle}{(E_i - E_v + \hbar\omega)^2} \right. \\
 & \left. + \sum_{vi'} \frac{\langle f|\epsilon \cdot D|v\rangle \langle v|\epsilon \cdot D|i'\rangle \langle i'|V|i\rangle}{(E_i - E_v + \hbar\omega)^2} \right] \quad (3)
 \end{aligned}$$

where the first term is the second-order contribution, and the second and third terms arise in third order. All states in this expression are eigenstates of the zero-order Hamiltonian (e.g. $H_0|i\rangle = E_i|i\rangle$), where the total Hamiltonian is

$$H = H_0 + V.$$

The details of this separation of H_0 and V hold the key to understanding the relationship between the various calculations.

In the usual many-body perturbation approach [7, 10], H_0 is the Hartree-Fock operator H_{HF} and V contains the non-central part of the Coulomb interaction V_{C} , the spin-orbit interaction V_{SO} , and the crystal-field interaction V_{CF} . (We do not consider the crystal-field interaction in this work.) It is well known [7, 10] that in this case there is a large cancellation between the second and third terms of (3). This cancellation removes 'unlinked' diagrams and gives rise to 'folded' diagrams that contain matrix elements of the Coulomb and spin-orbit interactions within the ground configuration.

Judd and Pooler [4], considering only the first two terms in (3), obtained an expression that contains 'unlinked' diagrams involving V_{SO} . Burdick and Reid [7] found that when the third term was added and the unlinked diagrams cancelled, the resulting calculations gave poor agreement with experiment, but that adding 'folded' Coulomb diagrams restored the agreement. This is not a coincidence, and may be understood by examining the third term in (3) carefully. In the cases of interest to us, if i and i' are eigenstates of H , then they are also eigenstates of V , and so the matrix element $\langle i'|V|i\rangle$ becomes $\delta(i, i')(E_i - E_i^0)$. That is, the effect of this term is to take into account the shift in energy of the ground-configuration states, caused by the perturbation V .

Alternatively, if we choose the Hamiltonian H_0 that acts within the ground configuration, H_{gr} , to include $H_{\text{HF}} + V$, then the third term of (3) will vanish, and there will be no folded diagrams in the expansion. This is the choice that the Judd-Pooler calculation implicitly makes, giving rise to unlinked diagrams. It is important to note, however, that H_{gr} is then fundamentally different from H_{ex} , the H_0 acting within the excited configuration, since we now have

$$H_{\text{gr}} = H_{\text{HF}} + V$$

whereas

$$H_{\text{ex}} = H_{\text{HF}}.$$

This means that the energy denominators must include the difference between the true states energies within the ground configuration and the zero-order energy of the excited configuration. This point does not appear to have been recognized by users of the Judd-Pooler theory, but it is important when comparing transitions over a wide range of energies.

If we use many-body perturbation theory, folded Coulomb and spin-orbit diagrams must be included. However, as shown by the above discussion, we would expect to get

similar results to the Judd–Pooler calculation. A fundamental difference between these two approaches will result from Coulomb interactions within the excited configuration—terms which were not included in [7].

Our direct calculation goes even further, explicitly including V in the Hamiltonian H_{ex} , as well as in H_{gr} . Hence, we have no third-order terms, since

$$H_0 = H_{HF} + H_C + H_{SO}$$

and there is no longer any V which is separate from H_0 . Thus, our direct calculation need only contain second-order contributions.

Free-ion Hartree–Fock parameters used in the wavefunction diagonalization and energy level calculation for states in the ground $4f^7$ and intermediate $4f^65d$ configurations were generated using atomic structure programs of Cowan [11], and are given in table 1. Cowan's RCG program [12] calculates one-photon atomic transition intensities between multiple configurations. Thus, it took only minor modification in order to generate one-photon electric-dipole matrix elements $\langle EJ || D^{(1)} || E''J'' \rangle$ between intermediate coupled states EJ of the configuration $4f^7$, and $E''J''$ of the configuration $4f^65d$. This allows us to evaluate (2) explicitly for each transition considered.

Table 1. Free-ion Hartree–Fock parameters used in the wavefunction diagonalization and energy level calculation for states in the ground $4f^7$ and intermediate $4f^65d$ configurations of Eu^{2+} . All values are given in cm^{-1} .

E^0 ($4f^65d$)	66 000
F^2 (ff)	105 300
F^4 (ff)	65 900
F^6 (ff)	47 400
F^2 (dd)	27 800
F^4 (dd)	13 800
G^1 (fd)	13 800
G^3 (fd)	11 000
G^5 (fd)	8 300
ζ_f	1 420
ζ_d	1 150

If we ignore energy level splittings within the ground configuration, and take all energy denominators to be between the intermediate-state energy E'' within the excited configuration and the zero-order energy of the ground configuration, our direct calculation can imitate a perturbation expansion which neglects the bracketed third-order term of (3). Then, setting the Hamiltonian H_{ex} acting within the excited configuration equal to H_{HF} and $H_{HF} + H_{SO}$, respectively, we get relative line strength results similar to those presented by Downer and coworkers [5] for their second-order and third-order spin–orbit calculations. These results are presented in table 2 for relevant ${}^8S_{7/2} \rightarrow {}^6P_J$, 6D_J transitions. Transition intensities have been scaled with respect to the ${}^8S_{7/2} \rightarrow {}^6D_{9/2}$ transition for each row. The ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$, ${}^6D_{7/2}$ transitions are of particular interest. Whereas the second-order calculation underestimates the magnitude of these transitions, when spin–orbit contributions are included, these transitions are greatly overestimated, ${}^6P_{7/2}$ by a factor of more than 100 and ${}^6D_{7/2}$ by a factor of four.

In table 3, we present results obtained by including calculated energy level splittings within the ground configuration. By using these energies, we take into account the effects

Table 2. Relative line strengths for ${}^8S_{7/2} \rightarrow {}^6P_J, {}^6D_J$ two-photon absorption from a single linearly polarized beam. Energy level splittings within the ground configuration have been ignored in order to facilitate comparison with the calculations of [5]. Intermediate-state wavefunctions have been diagonalized with respect to different Hamiltonians, H_{ex} , which act upon the excited configuration. Experimental values are taken from [5].

	${}^6P_{7/2}$	${}^6P_{5/2}$	${}^6P_{3/2}$	${}^6D_{9/2}$	${}^6D_{7/2}$	${}^6D_{5/2,3/2}$
$H_{ex} = H_{HF}$	0.14	0.06	0.002	1.0	0.8	0.59
$H_{ex} = H_{HF} + H_{SO}$	97.9	0.26	0.091	1.0	5.4	0.52
Experiment	0.95	0.04	—	1.0	1.3	0.22

of Coulomb and spin-orbit interactions within the ground configuration. The second line of table 3, which includes spin-orbit effects within the excited configuration, most closely resembles our perturbation calculations for Gd^{3+} [7]. We find that inclusion of ground-configuration energy splittings produces a significant improvement in the fitting of this calculation to experiment. However, the ${}^6P_{7/2}$ transition is still overestimated by a factor of more than 20.

Table 3. Relative linearly polarized line strengths for ${}^8S_{7/2} \rightarrow {}^6P_J, {}^6D_J$ two-photon transitions, presented in the same format as table 2. Energy level splittings within the ground configuration are explicitly included. Experimental values are taken from [5].

	${}^6P_{7/2}$	${}^6P_{5/2}$	${}^6P_{3/2}$	${}^6D_{9/2}$	${}^6D_{7/2}$	${}^6D_{5/2,3/2}$
$H_{ex} = H_{HF}$	0.14	0.06	0.002	1.0	0.8	0.59
$H_{ex} = H_{HF} + H_{SO}$	21.8	0.13	0.028	1.0	2.2	0.55
$H_{ex} = H_{HF} + H_C$	35.0	0.005	0.015	1.0	3.9	0.68
$H_{ex} = H_{HF} + H_{SO} + H_C$	1.15	0.06	0.002	1.0	0.9	0.58
Experiment	0.95	0.04	—	1.0	1.3	0.22

The remaining correlation contributions, which act within the excited configuration, could be safely ignored in Gd^{3+} . However, for Eu^{2+} , the Coulomb splittings are large when compared to the interconfigurational energy gap, and cannot reasonably be ignored. When we include the Coulomb interaction within the excited configuration, the large experimental discrepancy is resolved, resulting in good agreement with the experimental measurements. This is presented in the last two rows of table 3. We are also able to achieve good agreement with experimental circularly polarized measurements. In particular, we calculate a factor of 5.2 decrease in circularly polarized intensity versus linear polarization for the ${}^6P_{7/2}$ transition, as compared to a 5.6-fold experimental decrease.

In conclusion, we have included correlation along with spin-orbit contributions in our direct two-photon absorption intensity calculations. This results in good agreement with experiment for the ${}^8S_{7/2} \rightarrow {}^6P_J, {}^6D_J$ transitions in Eu^{2+} for both linear and circular polarizations of the excitation beam. In order to compute the intensities of the remaining Eu^{2+} transitions measured by Downer *et al* [5], it will be necessary to incorporate crystal-field effects into our calculations.

The direct calculations presented here avoid the use of the closure approximation. Therefore, they should be able to provide two-photon intensity calculations throughout the divalent lanthanide series, a realm where inaccuracies in the closure approximation render perturbation calculations untenable.

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