Many-Body Perturbation Theory Calculations of Two-Photon Absorption in Lanthanide Compounds

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(Received 14 December 1992)

Third-order spin-orbit contributions to two-photon absorption rates were introduced by Judd and Pooler when the second-order theory was found to be inadequate to explain the experimental data for Gd^{3+} ions in LaF_3. However, only one of the two perturbation terms that arise in third order was considered. When the omitted term is added, "unlinked" parts are canceled and the good agreement with experiment is lost. Inclusion of previously overlooked scalar two-electron contributions can restore the agreement between theory and experiment.

PACS numbers: 78.50.Ec, 31.20.Tz, 34.80.Kw

In 1981 Dagenais *et al.* [1] made quantitative measurements of two-photon absorption probabilities within the $4f^7$ configuration of Gd^{3+} substituted for La^{3+} in LaF_3. The relative integrated intensities from the ground multiplet, ${}^8S_{7/2}$, to the ${}^6P_{7/2}$, ${}^6P_{5/2}$, and ${}^6P_{3/2}$ multiplets were found to be poorly reproduced by the standard second-order theory developed by Axe [2].

Judd and Pooler [3] pointed out that second-order contributions to these "spin-forbidden" transitions are unusually small, and calculated third-order contributions that include spin-orbit perturbations within intermediate states. These perturbations lead to spin-dependent operators, including a scalar operator that especially enhances the $\Delta J = 0$ transition ${}^8S_{7/2} \to {}^6P_{7/2}$. This idea was elaborated on by Downer and co-workers [4] and by other workers. Kibler and Gâcon [5] developed a symmetry-adapted formalism in which the scalar and rank-two contributions were handled phenomenologically. This approach was used to explain polarization dependencies of the $\Delta J = 0$, ${}^7F_0 \to {}^5D_0$ transition in Sm^{2+} and Eu^{3+} in various materials [6,7] in terms of interference effects between scalar and rank-two contributions. Third-order terms were also found to be important for spin-forbidden one-photon transitions [8]. However, a close examination of Judd and Pooler's calculations reveals a problem. They contain "unlinked" terms that are canceled in "many-body perturbation theory" [9–11].

Goldstone [9] used time-dependent perturbation theory and the adiabatic theorem to prove the cancellation of all unlinked terms in the perturbation expansion of the energy of a nondegenerate ground state. Over the years refined proofs have appeared, the nondegenerate condition has been removed, and many-body calculations have become standard in theoretical studies of nuclear, condensed matter, atomic, and molecular systems [10,11].

Many-body calculations often employ the concept of a "model space." Rather than solving for the eigenvalues and eigenstates of the full Hamiltonian, an "effective Hamiltonian" is diagonalized within the model space, and the expectation values of "effective operators" are evaluated between the model-space eigenvectors [10,11]. In this paper we use the notation of Lindgren and Morrison [10]. In extending the formalism to include atom-photon interactions the energy denominators are modified by the inclusion of photon energies [12,13].

Ng and co-workers have applied many-body techniques to the calculation of energy levels [14,15] and one- and two-photon transition intensities [16] of lanthanide ions in solids. The numerical calculations were only taken to second order, but Ng and Newman [14] list all third-order diagrams. Ignoring diagrams involving core states and assuming two photons of identical energy ω ($\hbar = 1$), we have only one second-order diagram and two third-order diagrams involving the spin-orbit interaction V_{so} and the dipole moment $\mathbf{r}$. These are shown in Figs. 1(a)–1(c), and have algebraic expressions

$$a_k^\dagger a_i \sum_s \frac{\langle k|\mathbf{r}|s\rangle\langle s|\mathbf{r}|i\rangle}{\varepsilon_i - \varepsilon_s + \omega}, \tag{1}$$

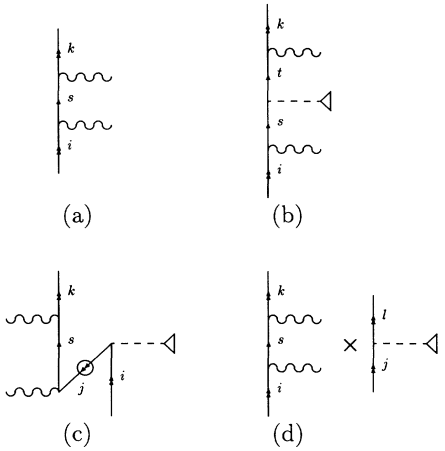

FIG. 1. Second- and third-order one-electron two-photon absorption diagrams. For details of notation see Ref. [10]. A single up-going arrow represents a virtual orbital; a double arrow a valence orbital. Folded valence lines have a circle around their arrows. Photons are represented by wavy lines and the spin-orbit interaction by a triangle. Diagrams (a), (b), and (c) correspond to Eqs. (1), (2), and (3) of the text, respectively. Diagram (c) is folded; diagram (d) is unlinked.

$$a_k^\dagger a_i \sum_{st} \frac{\langle k|\mathbf{r}|t\rangle\langle t|V_{so}|s\rangle\langle s|\mathbf{r}|i\rangle}{(\varepsilon_i - \varepsilon_t + \omega)(\varepsilon_i - \varepsilon_s + \omega)}\,, \tag{2}$$

$$-\,a_k^\dagger a_i \sum_{js} \frac{\langle k|\mathbf{r}|s\rangle\langle s|\mathbf{r}|j\rangle\langle j|V_{so}|i\rangle}{(\varepsilon_i - \varepsilon_s + \omega)(\varepsilon_j - \varepsilon_s + \omega)}\,. \tag{3}$$

In these expressions, i, j, and k label valence ($4f$) orbitals in our (initially degenerate) $4f^N$ model space, s and t label virtual orbitals outside the model space (nd or ng), and the ε are orbital energies. Each term contains a product of a creation operator and an annihilation operator for $4f$ orbitals. The diagram corresponding to Eq. (3) [Fig. 1(c)] is commonly referred to as "folded" [10,11].

Judd and Pooler [3] have expressions equivalent to Eqs. (1) and (2), but instead of Eq. (3) they have an unlinked expression involving products of operators acting on two different electrons [Fig. 1(d)]. This is because they omit one of the terms required in third order. Using states of the $4f^N$ and $4f^{N-1}5d$ *configurations*, as opposed to the *orbitals* used in Eqs. (1)–(3), we add this neglected term to their Eq. (3) to obtain

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

$$-\sum_{JS} \frac{\langle K|\mathbf{r}|S\rangle\langle S|\mathbf{r}|J\rangle\langle J|V_{so}|I\rangle}{(E_J - E_S + \omega)(E_I - E_S + \omega)}\,, \tag{4}$$

where I, J, and K label states of the $4f^N$ configuration, and S and T states of the $4f^{N-1}5d$ configuration. The unlinked diagram arising from the first sum of Eq. (4) is canceled by the second, leaving Eq. (2) from the first and Eq. (3) from the second [10].

The effective one-electron operator for two-photon absorption may be written in terms of standard $\mathbf{U}^{(k)}$ and $\mathbf{W}^{(1k)k'}$ tensors [6]. For the "second-order" and "third-order spin-orbit" contributions we have

$$V_{\mathrm{TPA}}^{2} = C_{[2]}\mathbf{U}^{(2)} \cdot (\epsilon_1\epsilon_2)^{(2)} \tag{5}$$

$$V_{\mathrm{TPA}}^{3S} = C_{[(11)0]}\mathbf{W}^{(11)0} \cdot (\epsilon_1\epsilon_2)^{(0)} + (C_{[(11)2]}\mathbf{W}^{(11)2} + C_{[(13)2]}\mathbf{W}^{(13)2}) \cdot (\epsilon_1\epsilon_2)^{(2)}\,, \tag{6}$$

where $(\epsilon_1\epsilon_2)^{(K)}$ is a coupled product of the polarization vectors of the photons. Notice that all the radiation polarization dependence is contained in the $(\epsilon_1\epsilon_2)^{(K)}$. In particular, for single-beam circular polarized light, $(\epsilon_1\epsilon_2)^{(0)} = 0$. Only for $C_{[(11)0]}$ does our evaluation differ from Judd and Pooler [3]. Their unlinked terms lead to the tensor product $\mathbf{U}^{(0)}\mathbf{W}^{(11)0}$, proportional to $\mathbf{W}^{(11)0}$, which enhances the $C_{[(11)0]}$ parameter. When the virtual orbital is $5d$, Judd and Pooler's "unlinked" result is

$$C_{[(11)0]}^{U} = \mathcal{R}\,[2\zeta_{5d}/3 + (N-1)\zeta_{4f}]\,, \tag{7}$$

where $\mathcal{R} = \frac{2\sqrt{2}}{\sqrt{7}}\langle 5d|\mathrm{r}|4f\rangle^2/(\varepsilon_{4f} - \varepsilon_{5d})^2$, and N is the number of $4f$ electrons (7 for Gd^{3+}). In contrast, we obtain the "linked" result

$$C_{[(11)0]}^{L} = \mathcal{R}[2\zeta_{5d}/3 + (-1)\zeta_{4f}]\,. \tag{8}$$

This differs from Eq. (7) by the removal of N, which dramatically reduces $C_{[(11)0]}$, and with it the enhancement of the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition used by Judd and Pooler to explain the experimental data. In order to recover good agreement with experiment we shall have to find another contribution, scalar in J, to selectively enhance the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition.

It has been shown that third-order perturbations including the Coulomb interaction lead to many-electron "correlation" effects that have a large influence on one- and two-photon transition intensities in lanthanide compounds [17]. The effective one-electron contributions considered in Ref. [17] cannot affect the relative intensities of the transitions considered here, since they merely scale the $C_{[2]}$ parameter, but two-body scalar operators can selectively enhance the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition. Two-electron "third-order correlation" contributions to two-photon absorption have the form

$$V_{\mathrm{TPA}}^{3C} = \sum_{k_1 \le k_2, K} D_{[(k_1k_2)K]}\mathbf{U}^{(k_1k_2)K} \cdot (\epsilon_1\epsilon_2)^{(K)}\,, \tag{9}$$

where $\mathbf{U}^{(k_1k_2)K} \equiv \sum_{i<j}[\mathbf{u}(i)^{(k_1)}\mathbf{u}(j)^{(k_2)}]^{(K)}$ is a two-electron operator. The i,j sum is over the $4f$ electrons. For the absorption of two photons of the same energy, K is restricted to 0 or 2. Though a scalar one-electron operator (i.e., $\mathbf{U}^{(0)}$) is a constant and therefore cannot induce *transitions*, there is no such restriction on two-electron operators (except when $k_1 = k_2 = 0$). In calculating contributions to the $D_{[(k_1k_2)K]}$ parameters it is important to avoid overcounting the scalar central potential used in the zero-order Hamiltonian [10,17].

We present the third-order two-photon, two-electron diagrams in Fig. 2, where for clarity we have omitted the diagrams involving excitation of core orbitals as well as the diagrams which are Hermitian conjugates of Figs. 2(b) and 2(d). Folded diagram 2(e) is non-Hermitian (this is a general property of many-body Hamiltonians [10]). In our calculation we Hermitize it by averaging it with its Hermitian conjugate. This folded diagram dominates because the radial integrals $R^k(4f4f, 4f4f)$ are significantly larger than the R^k for nonequivalent orbitals. In fact, the $R^k(4f4f, 4f4f)$ are the same order of magnitude as the energy denominators, $\varepsilon_{4f} - \varepsilon_{5d}$, and consideration of higher orders is necessary to achieve convergence. This slowness of convergence is unique to these folded diagram contributions to intensities and does not affect calculations of the effective Hamiltonian, such as calculations of the Slater parameters [10,18], because in that case the dominant effects involve the excitation of two electrons, and therefore larger denominators. For transition intensity calculations it may be preferable to expand the model space to include both $4f^N$ and $4f^{N-1}d$, in analogy to the calculation of the ground-state energy of beryllium [10], an idea that has been considered [19,20].

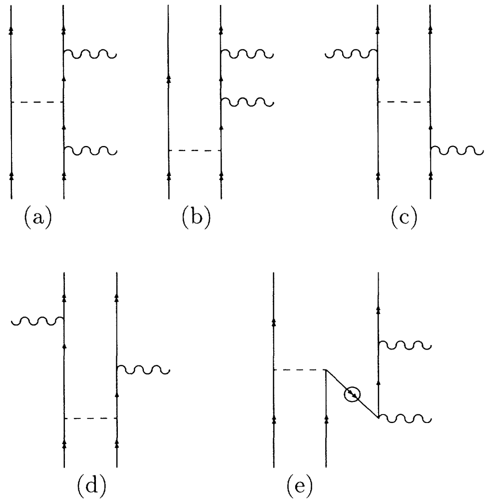

FIG. 2. Some third-order two-electron two-photon absorption diagrams. The notation is the same as Fig. 1. The Coulomb interaction is represented by a dotted line. Folded diagram (e) dominates our correlation calculation.

In presenting our calculations, we restrict ourselves to total intensities for two photons of the same linear polarization, summed over J multiplets. In this case the $K = 0$ and $K = 2$ contributions may be evaluated separately. For each K we sum the products of the reduced matrix elements with the respective parameters, square the result, and multiply by the appropriate factors (1/3 for $K = 0$ and 2/15 for $K = 2$) arising from the polarization tensor $(\epsilon_1\epsilon_2)^{(K)}$ and the summation over the M_J components. In Table I we list the reduced matrix elements relevant to our discussion, calculated using the parameters given by Carnall *et al.* [21] for Gd^{3+}:LaF_3. Numerical calculations of the perturbation expressions were done using Hartree-Fock-Slater orbitals, generated in a finite box to avoid the necessity of using continuum states [22]. Parameters given in Table I were calculated considering only the $4f^65d$ excited configuration. In extending the calculation to include all allowed configurations we find that other d-orbital contributions, including core excitations, are negligible, and g orbitals provide a total contribution of less than 15% of the $4f^65d$ contribution.

Coulomb correlation parameters, $D_{[(k_1k_2)K]}$, are listed in Table I only for the dominant folded diagram [Fig. 2(e)]. By adding successive folded Coulomb perturbations, we have estimated a summation to infinite order. To do a complete evaluation of the remaining correlation contribution, we have to calculate not only the rest of the the third-order Coulomb diagrams, but also fourth-order diagrams involving both the spin-orbit and Coulomb interactions. Also, due to the slowness of convergence, terms involving $R^k(4f4f,4f4f)$ radial integrals must be taken to even higher orders. We have carried out an extensive evaluation of these diagrams. The contributions are not particularly large relative to Fig. 2(e). However, the Coulomb and spin-orbit contributions tend to cancel so the results are quite sensitive to the order to which the calculation is taken.

Calculations of transition intensities are presented in Table II. Each row gives relative intensities, scaled to the $^8S_{7/2} \to {}^6P_{3/2}$ transition. Although the "unlinked" expression used by Judd and Pooler provides a good fit to the experiment, we find that considering only second-order and linked third-order spin-orbit terms (line 3) greatly underestimates the $^8S_{7/2} \to {}^6P_{7/2}$ transition. As shown in the fourth line, when we consider second-order and third-order Coulomb terms, the $^8S_{7/2} \to {}^6P_{5/2}$ transition is greatly underestimated. However, when we add both spin-orbit and Coulomb terms to the second-order

TABLE I. Reduced matrix elements of the operators used in Eqs. (5), (6), and (9) between the $^8S_{7/2}$ multiplet and the ^6P_J multiplets of Gd^{3+}, together with calculated parameters. Note that the $\mathbf{U}^{(k_1k_2)K}$ are two-electron operators. Parameters are scaled so that $C_{[2]} = 1$.

	Reduced matrix elements				
Operator	$\langle{}^6P_{3/2}\|\| \;\|\|{}^8S_{7/2}\rangle$	$\langle{}^6P_{5/2}\|\| \;\|\|{}^8S_{7/2}\rangle$	$\langle{}^6P_{7/2}\|\| \;\|\|{}^8S_{7/2}\rangle$	Parameters	
$\mathbf{U}^{(2)}$	0.0033	0.0177	−0.0278	$C_{[2]}$	1
$\mathbf{W}^{(11)0}$	0	0	−1.5645	$C_{[(11)0]}$	−0.015[a]
$\mathbf{W}^{(11)2}$	2.2288	2.1060	−1.5262	$C_{[(11)2]}$	0.0052
$\mathbf{W}^{(13)2}$	−0.0070	−0.0077	−0.0285	$C_{[(13)2]}$	−0.0039
$\mathbf{U}^{(22)0}$	0	0	−0.0067	$D_{[(22)0]}$	1.89
$\mathbf{U}^{(44)0}$	0	0	−0.0162	$D_{[(44)0]}$	1.45
$\mathbf{U}^{(66)0}$	0	0	−0.0272	$D_{[(66)0]}$	2.21
$\mathbf{U}^{(02)2}$	0.0037	0.0200	−0.0315	$D_{[(02)2]}$	0.19
$\mathbf{U}^{(22)2}$	−0.0054	−0.0040	0.0020	$D_{[(22)2]}$	−0.35
$\mathbf{U}^{(24)2}$	−0.0004	−0.0015	0.0018	$D_{[(24)2]}$	0.92
$\mathbf{U}^{(44)2}$	−0.0144	−0.0139	0.0106	$D_{[(44)2]}$	0.07
$\mathbf{U}^{(46)2}$	−0.0002	−0.0006	0.0005	$D_{[(46)2]}$	0.41
$\mathbf{U}^{(66)2}$	−0.0249	−0.0251	0.0194	$D_{[(66)2]}$	0.88

[a] This value is obtained using the linked expression, Eq. (8). For the unlinked expression, Eq. (7), we obtain 0.142.

TABLE II. Multiplet-multiplet intensities for two-photon absorption in Gd^{3+}:LaF_3. Each row is independently scaled to the $^8S_{7/2} \rightarrow {}^6P_{3/2}$ transition.

	$^8S_{7/2} \rightarrow {}^6P_{3/2}$	$^8S_{7/2} \rightarrow {}^6P_{5/2}$	$^8S_{7/2} \rightarrow {}^6P_{7/2}$
Experiment	1	5.4	320
Second-order	1	29	71
Second-order and third-order spin-orbit	1	3.7	12.[a]
Second-order and two-electron	1	0.011	76
Second-order, spin-orbit, and two-electron	1	2.4	397

[a] This value is for the linked expression for $C_{[(11)0]}$. With the unlinked expression this intensity is 557.

terms (line 5) a good fit to experiment is restored. We have also carried out calculations for individual Stark components and for circular polarization. Though our calculations include two-body operators, the relative balance of rank-zero and rank-two operators is approximately the same as in previous calculations [4], and therefore the results are not very different.

This work may have significant implications for calculations of other lanthanide and actinide transitions. We expect the greatest observable consequences of correlation to arise in comparisons between transitions extending over a wide range of energy values, and for those ions with low-lying excited configurations, where large Coulomb contributions can cause significant breakdown of the conventional closure approximation, an idea previously discussed by Downer *et al.* for Eu^{2+} ions [23]. It should be noted that most recent work (e.g., Ref. [6]) has concentrated on the interesting polarization effects arising from the interference between rank-zero (scalar) and rank-two operators, and does not distinguish between rank-zero spin-orbit and rank-zero correlation operators. We have not yet included the crystal-field effects required to explain transitions for which $\Delta J > 2$ [4]. This will be necessary for a complete treatment of the Gd^{3+} two-photon spectrum.

As well as two-photon absorption, Raman scattering and one-photon transitions may have large correlation contributions. In the case of Raman scattering, these contributions may affect the asymmetry ratios that have proved so difficult to calculate accurately [19]. For one-photon transitions, calculations of the spin-orbit contributions [8] will be modified and correlation effects added. However, for most one-photon transitions where the $\mathbf{W}^{(11)0}$ or $\mathbf{U}^{(k_1k_2)0}$ terms would be important, there are dominant magnetic-dipole matrix elements. A notable exception is the $^7F_0 \rightarrow {}^5D_0$ transition in Eu^{3+} and Sm^{2+} [24]. It appears that correlation will also result in large nonscalar two-electron terms, and the one-electron parametrizations that have provided the basis for interpretation of one- and two-photon transition intensities in lanthanide ions [16] may need to be reconsidered. We note that the effects of spin-orbit and Coulomb perturbations on transition intensities were discussed by Wybourne [25] many years ago.

We wish to acknowledge the hospitality of Xia Shang-Da and the University of Science and Technology of China during the formative period of this work. We thank H. J. Kooy, Jr., for supplying the computer software used to generate our diagrams.

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