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Transition amplitude calculations for one- and two-photon absorption

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Abstract

We apply known many-body perturbation techniques to the calculation of one- and two-photon transition intensities within the f^N configurations of lanthanide and actinide ions. We demonstrate how to construct linked expressions to third order. For one-photon electric–dipole transitions the only one-electron spin-independent effective operators needed are those of even rank. © 1998 Elsevier Science S.A.

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1. Introduction

The theory of one-photon absorption in rare earth compounds was developed by Judd [1] and Ofelt [2] in 1962, and has become known as the Judd–Ofelt theory. This theory was extended to the case of two-photon absorption by Axe [3] in 1964, who considered only the second-order terms. More recently, it has become possible to observe transitions for which the second-order terms give an unusually small contribution, so that it has been necessary to extend the calculations to third order and higher [4]. Judd and Pooler [5], Burdick, Downer and Sandar [6] and Smentek–Mielczarek and Hess [7] have carried out calculations involving these higher order terms.

However, at third order and above the number of possible expressions in the perturbation expansion becomes large, and it is important to keep careful track of them in order to avoid overcounting or missing terms. Many-body perturbation theory is highly developed and provides a systematic method of doing this. It has been an important computational tool in atomic, molecular, and condensed matter physics. A key concept in such calculations is the linked cluster theorem which was proven by Goldstone in 1957 [8]. The linked cluster theorem implies that unlinked terms must cancel. If they did not, then energies would have unreasonable dependencies on the number of particles in the system. Brandow has proved [9] that the linked cluster theorem holds for the matrix elements of any effective operator, provided that care is taken with the normalisation of the states.

Hurtubise and Freed [10] have constructed a perturbation expansion for dipole moment operators relevant to one-photon absorption. They have verified that this expansion is linked up to third order.

Burdick and Reid [11,12] pointed out that the two-photon calculations of Judd and Pooler [5] would lead to unlinked terms in a many-body expansion (the symptom of this is the appearance of a factor of N in Judd and Pooler's Eq. (16)). They claimed instead that it was possible to carry out a calculation analogous to the standard calculation, but which incorporated the dipole moment operator from the standard theory of two-photon transitions in place of some of the time-independent perturbation operators.

In this work we review the calculations of Hurtubise and Freed and of Burdick and Reid and comment on the application of many body techniques to rare-earth transition intensities. We also comment on the relationship to phenomenological models [13]. One knows from time reversal and hermiticity symmetries that the (one particle) crystal field within an f^N configuration is parameterised by only even rank operators [14]. We argue that the same result applies to the parameterisation of one-photon electric dipole transitions.

2. Model spaces and true wavefunctions

We use a notation which is similar to that of Hurtubise and Freed. The Hamiltonian is partitioned into

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$$H = H_0 + V \tag{1}$$

We shall represent an exact state (which is the eigenfunction of the complete hamiltonian) by $|k\rangle$. Thus

$$H|k\rangle = E_k|k\rangle \tag{2}$$

Eigenstates of H_0, which are not necessarily eigenstates of H, are denoted by $|k'\rangle$. Thus

$$H_0|k'\rangle = E^{(0)}_{k'}|k'\rangle \tag{3}$$

We define a model space, with projection operator P. This will usually be the f^N configuration in applications of interest here. In this space the effective Hamiltonian, h, has the same eigenvalues as the full Hamiltonian H, with eigenstates $|k\rangle_0$. That is,

$$h|k\rangle_0 = E_k|k\rangle_0 \tag{4}$$

The projection operator for the orthogonal space is Q.

In many MBPT applications only the energies are of interest, and the normalisation of the states is not important. Consequently, the normalisation chosen for many MBPT calculations is the intermediate normalisation convention (${}_0\langle i|j\rangle_0 = \delta_{ij}$, $\langle i|j\rangle_0 = \delta_{ij}$), as this simplifies the calculation. However, in the calculation of expectation values or transition intensities, it is highly desirable to use norm preserving transformations [15] so that $\langle i|j\rangle = \delta_{ij}$.

Brandow has shown [9,16] that the norm-preserving transformation between the exact and model states is given by

$$|i\rangle = \hat{k}|i\rangle_0 \tag{5}$$

where

$$\hat{k} = \Omega(\Omega^\dagger\Omega)^{-1/2}, \tag{6}$$

and Ω is the wave operator used by Lindgren and Morrison [17]. The $(\Omega^\dagger\Omega)^{-1/2}$ factor is necessary to ensure that the full wavefunction $|i\rangle$ is normalised.

In the following we use the symbol D to represent a general multipole operator (usually the electric dipole operator). The transition amplitude for one-photon absorption is proportional to

$$\langle f|D|i\rangle \tag{7}$$

Similarly, the transition amplitude for two-photon absorption is proportional to

$$\sum_k \frac{\langle f|D_2|k\rangle\langle k|D_1|i\rangle}{E_i - E_k + \hbar\omega_1} + \sum_k \frac{\langle f|D_1|k\rangle\langle k|D_2|i\rangle}{E_i - E_k + \hbar\omega_2} \tag{8}$$

where $\hbar\omega_1$, $\hbar\omega_2$ are the energies of the two photons. This formula may also be applied to Raman scattering if a minus sign is associated with the $\hbar\omega$ of the outgoing photon.

We shall define the order of any particular term to be the total number of D and V operators in its numerator. Thus expression (11) is a second order expression, while expression (13) is third order. An alternative is to refer to (11) as first order in V, and to (13) as second order in V, as Hurtubise and Freed [10] do in their various papers.

The exact states in expressions (7) and (8) are time-independent, so we may calculate them using time-independent perturbation theory. Brandow [9,16] and Hurtubise and Freed [15] have provided the underlying algebra for calculations of this sort.

3. One-photon absorption

We may expand the exact states in expression (7) above using the $\hat{k}$'s of the previous section, which gives us

$${}_0\langle f|\hat{k}^\dagger D\hat{k}|i\rangle_0 \tag{9}$$

We note that the operator $\hat{k}^\dagger D\hat{k}$ is Hermitian order by order [15] and if it is also time-reversal even (e.g., the electric dipole moment) then standard arguments [18,19] imply that the one-electron spin-independent part consists of even-rank tensors. However, it is possible to have two-body, or spin-dependent operators with odd rank, as in the case of the correlation crystal field [18].

Expression (9) is exact. We may now use perturbation theory to expand $\hat{k}$ to any desired order. The result of carrying out this expansion is

$$\langle f|D|i\rangle = {}_0\langle f|D|i\rangle_0 \tag{10}$$

$$+ \sum_{k'\in Q} \frac{{}_0\langle f|V|k'\rangle\langle k'|D|i\rangle_0}{E^{(0)}_f - E^{(0)}_{k'}} \tag{11}$$

$$+ \sum_{k'\in Q} \frac{{}_0\langle f|D|k'\rangle\langle k'|V|i\rangle_0}{E^{(0)}_i - E^{(0)}_{k'}} \tag{12}$$

$$+ \sum_{r'\in Q}\sum_{k'\in Q} \frac{{}_0\langle f|V|r'\rangle\langle r'|D|k'\rangle\langle k'|V|i\rangle_0}{(E^{(0)}_f - E^{(0)}_{r'})(E^{(0)}_i - E^{(0)}_{k'})} \tag{13}$$

$$+ \sum_{r'\in Q}\sum_{k'\in Q} \frac{{}_0\langle f|V|r'\rangle\langle r'|V|k'\rangle\langle k'|D|i\rangle_0}{(E^{(0)}_f - E^{(0)}_{r'})(E^{(0)}_f - E^{(0)}_{k'})} \tag{14}$$

$$+ \sum_{r'\in Q}\sum_{k'\in Q} \frac{{}_0\langle f|D|r'\rangle\langle r'|V|k'\rangle\langle k'|V|i\rangle_0}{(E^{(0)}_i - E^{(0)}_{r'})(E^{(0)}_i - E^{(0)}_{k'})} \tag{15}$$

$$- \sum_{k'\in Q}\sum_{j'\in P} \frac{{}_0\langle f|V|j'\rangle\langle j'|V|k'\rangle\langle k'|D|i\rangle_0}{(E^{(0)}_f - E^{(0)}_{k'})(E^{(0)}_{j'} - E^{(0)}_{k'})} \tag{16}$$

$$- \sum_{k'\in Q}\sum_{j'\in P} \frac{{}_0\langle f|D^x|k'\rangle\langle k'|V|j'\rangle\langle j'|V|i\rangle_0}{(E^{(0)}_i - E^{(0)}_{k'})(E^{(0)}_{j'} - E^{(0)}_{k'})} \tag{17}$$

$$- \frac{1}{2}\sum_{k'\in Q}\sum_{j'\in P} \frac{{}_0\langle f|V|k'\rangle\langle k'|V|j'\rangle\langle j'|D|i\rangle_0}{(E^{(0)}_f - E^{(0)}_{k'})(E^{(0)}_{j'} - E^{(0)}_{k'})} \tag{18}$$

$$- \frac{1}{2}\sum_{k'\in Q}\sum_{j'\in P} \frac{{}_0\langle f|D|j'\rangle\langle j'|V|k'\rangle\langle k'|V|i\rangle_0}{(E^{(0)}_{j'} - E^{(0)}_{k'})(E^{(0)}_i - E^{(0)}_{k'})} \tag{19}$$

Note that the ''normalisation'' terms (18) and (19) arise from the expansion of the $(\Omega^{\dagger}\Omega)^{-1/2}$ component of $\hat{k}$. Thus we see that to first order in V, the expansion may be generated by replacing one of the V's by a D in the standard perturbation theory expansion for the effective hamiltonian. However, this is not the case at higher order.

Note also that the two expressions (11) and (12) are the standard Judd–Ofelt [1,2] expressions. In the case where the model space is degenerate (which is the obvious choice for the f^N configuration) the two denominators are equal. In the context of the present work it is seen that Judd's closure approximation is equivalent to the truncation of the expansion at first order in V. Relaxation of this closure approximation is equivalent to evaluating higher-order terms in the model space calculation.

4. Two-photon absorption

In the case of two-photon absorption, we use expression (8) to calculate the transition amplitudes. Here we shall consider only transitions within the same shell, so that the model spaces for the initial and final states are the same. (If we wish to consider inter-shell transitions, such as f→d, then the initial and final states will have separate model spaces.)

Expression (8) has exact energies in its denominator. It is necessary to convert these energies into zero-order energies if the linked cluster theorem is to work order-by-order. Therefore we expand the exact energies using

$$E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)} + \cdots \tag{20}$$

Thus we may expand $(E_i - E_k + \hbar\omega)^{-1}$ to give

$$\frac{1}{E_i - E_k + \hbar\omega} = \frac{1 + \frac{E_k^{(1)} - E_i^{(1)} + E_k^{(2)} - E_i^{(2)} + \cdots}{E_i^{(0)} - E_k^{(0)} + \hbar\omega} + \left(\frac{E_k^{(1)} - E_i^{(1)} + E_k^{(2)} - E_i^{(2)} + \cdots}{E_i^{(0)} - E_k^{(0)} + \hbar\omega}\right)^2 + \cdots}{(E_i^{(0)} - E_k^{(0)} + \hbar\omega)} \tag{21}$$

Now, $E_k^{(1)}$ is just ${}_0\langle k|V|k\rangle_0$. We are now in a position to expand expression (8). For brevity we consider the situation $\omega_1 = \omega_2 = \omega$, in which case there is only one term. To third order, this expansion is

$$\sum_k \frac{\langle f|D|k\rangle\langle k|D|i\rangle}{E_i - E_k + \hbar\omega} \tag{22}$$

$$= \sum_k \frac{{}_0\langle f|D|k\rangle_{00}\langle k|D|i\rangle_0}{E_i^{(0)} - E_k^{(0)} + \hbar\omega} \tag{23}$$

$$+ \sum_k \frac{{}_0\langle f|D|k\rangle_{00}\langle k|D|i\rangle_0}{E_i^{(0)} - E_k^{(0)} + \hbar\omega}\left[\frac{{}_0\langle k|V|k\rangle_0}{E_i^{(0)} - E_k^{(0)} + \hbar\omega}\right] \tag{24}$$

$$- \sum_k \frac{{}_0\langle f|D|k\rangle_{00}\langle k|D|i\rangle_0}{E_i^{(0)} - E_k^{(0)} + \hbar\omega}\left[\frac{{}_0\langle i|V|i\rangle_0}{E_i^{(0)} - E_k^{(0)} + \hbar\omega}\right] \tag{25}$$

$$+ \sum_k \sum_{r' \in Q_f} \frac{{}_0\langle f|V|r'\rangle\langle r'|D|k\rangle_{00}\langle k|D|i\rangle_0}{(E_i^{(0)} - E_k^{(0)} + \hbar\omega)(E_f^{(0)} - E_{r'}^{(0)})} \tag{26}$$

$$+ \sum_k \sum_{r' \in Q_k} \frac{{}_0\langle f|D|r'\rangle\langle r'|V|k\rangle_{00}\langle k|D|i\rangle_0}{(E_i^{(0)} - E_k^{(0)} + \hbar\omega)(E_k^{(0)} - E_{r'}^{(0)})} \tag{27}$$

$$+ \sum_k \sum_{r' \in Q_k} \frac{{}_0\langle f|D|k\rangle_{00}\langle k|V|r'\rangle\langle r'|D|i\rangle_0}{(E_i^{(0)} - E_k^{(0)} + \hbar\omega)(E_k^{(0)} - E_{r'}^{(0)})} \tag{28}$$

$$+ \sum_k \sum_{r' \in Q_i} \frac{{}_0\langle f|D|k\rangle_{00}\langle k|D|r'\rangle\langle r'|V|i\rangle_0}{(E_i^{(0)} - E_k^{(0)} + \hbar\omega)(E_i^{(0)} - E_{r'}^{(0)})} \tag{29}$$

Note that in this expansion terms (24) and (25) have arisen from the expansion of the exact energies in the denominator of expression (8). However, there are no terms equivalent to terms (18) and (19) in the expansion of the one-photon transition rate above. This is because these terms arise from the $(\Omega^{\dagger}\Omega)^{-1/2}$ factor of $\hat{k}$, which must be of at least second order in V, and therefore cannot have any contribution to two-photon terms of lower than fourth order (second order in V).

The expansion (23)–(29) can be simplified. In particular, with some manipulation of the denominators and summations, we may combine terms (24), (27) and (28). The resulting combined term is

$$\sum_{kj} \frac{{}_0\langle f|D|j\rangle_{00}\langle j|V|k\rangle_{00}\langle k|D|i\rangle_0}{(E_i^{(0)} - E_j^{(0)} + \hbar\omega)(E_i^{(0)} - E_k^{(0)} + \hbar\omega)} \tag{30}$$

where both k and j run over the entire Hilbert space. We may also convert term (25) so that it contains a summation over basis states in place of the $|i\rangle_{00}\langle i|$. The resulting term is

$$-\sum_{k'j'} \frac{{}_0\langle f|D|k'\rangle\langle k'|D|j'\rangle\langle j'|V|i\rangle_0}{(E_{j'}^{(0)} - E_{k'}^{(0)} + \hbar\omega)(E_i^{(0)} - E_{k'}^{(0)} + \hbar\omega)}. \tag{31}$$

The completeness theorem allows us to replace any summation over model functions $\Sigma_j\ |j\rangle_{00}\langle j|$ with a corresponding summation over basis functions $\Sigma_{j'}\ |j'\rangle\langle j'|$. This means that all of the summations over the entire Hilbert space in the expansion (23)–(29) and in terms (30) and (31) may be converted between model and basis function summations as is convenient.

Burdick and Reid [11,12] have considered the case where the model space is f^N and D is the electric dipole operator. In the particular case which they investigated some of the terms in expansion (23)–(29) are eliminated. The expressions used by Burdick and Reid are in agreement with our derivation for that particular case. However, in general their implication that it is possible to generate the transition rate expansion by all permutations of replacing two of the V's with D's in the energy expansion is not correct.

Often we will want to consider separately the case where the projection of $|k\rangle$ is in the model space P and the case where it is not in the model space. This should not present any special problems, provided that we are careful about the choice of our model and orthogonal spaces.

When the projection of $|k\rangle$ is in the model space it will generally be more convenient to perform the calculation as if it were a product of two one-photon processes (using expression (8) directly) since then we will be able to treat more easily any resonance effects which may occur. (These resonance effects are dependent upon the exact energies in the denominator.) In practice this will involve the use of the expansion for one-photon transition rates (10)–(19) to calculate each one-photon part of the expression.

Conversely, when the projection of $|k\rangle$ is in the orthogonal space, it will be most convenient to use the expansion derived above for two-photon absorption transition rates. This will avoid the direct calculation of exact energies except where it is absolutely necessary (as in the resonance case outlined above).

The determination of the restrictions on the ranks of parameters is quite complicated and depends on whether or not the two-photons have the same energy. Note that, unlike the expression for one-photon absorption, the expression for two-photon absorption is not necessarily Hermitian. However, if both photons have the same energy then only even rank one-electron spin-independent terms arise [4].

5. Linked cluster theorem

The transition moment expressions given above can be represented by diagrams analogous to those of Feynman. A closed diagram is one where the only electrons being absorbed and emitted by the process are valence electrons. A diagram is called disconnected if it contains two or more parts which are not connected by any interaction. If any of the parts of a disconnected diagram are closed, then the diagram is called unlinked. Thus an unlinked term is one where two or more valence electrons are being operated upon and each interaction (D or V) only acts on one of the electrons. Unlinked terms are undesirable as they lead to unreasonable dependencies on the number of particles. The linked cluster theorem shows that unlinked terms always cancel, and therefore do not need to be included in calculations.

The expansions given in sections 3 and 4 are linked to third order. Brandow has shown [9] that any n-body effective operator must be linked. In the case of one-photon absorption, $k^{\dagger}Dk$ is an effective operator and so must be linked. Similarly,

$$\sum_j \frac{\hat{k}^{\dagger}D|j\rangle\langle j|D\hat{k}}{H-E_j+\hbar\omega} \tag{32}$$

is the effective operator for two-photon absorption and consequently must also be linked. However, the derivation of a systematic expansion of this operator to all orders is not straightforward.

6. Conclusions

We have constructed a consistent perturbation theory derivation for one- and two-photon absorption transition rates. This is based on the expansion of the exact states in the expression for the transition moments. In general the one- and two-photon transition moment expansions cannot be generated by simple substitution of some of the V operators by D in the Rayleigh–Schrödinger energy expansion. While the operator substitution works for first and second order terms, it breaks down for third and higher order terms.

We have argued that the one-electron spin-independent part of the effective operator for one-photon electric–dipole transitions within the f^N configuration consists only of even-rank tensors. This has important implications in the phenomenological modelling of transition intensities.

References

[1] B.R. Judd, Phys. Rev. 127 (1962) 750.
[2] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[3] J.D. Axe, Phys. Rev. 136 (1964) A42.
[4] M.C. Downer, in: W.M. Yen (Ed.), Laser Spectroscopy of Solids II, vol. 65 of Topics in Applied Physics, Berlin, Springer-Verlag, 1989, pp. 29–75.
[5] B.R. Judd, D.R. Pooler, J. Phys. C: Solid State Phys. 15 (1982) 591.
[6] G.W. Burdick, M.C. Downer, D.K. Sardar, J. Chem. Phys. 91 (1989) 1511.
[7] L. Smentek-Mielczarek, B.A. Hess, J. Chem. Phys. 89 (1988) 703.
[8] J. Goldstone, Proc. R. Soc. 239 (1957) 267.
[9] B.H. Brandow, Rev. Mod. Phys. 39 (1967) 771.
[10] V. Hurtubise, K.F. Freed, J. Chem. Phys. 100 (1994) 4955.
[11] G.W. Burdick, M.F. Reid, Phys. Rev. Lett. 70 (1993) 2491.
[12] G.W. Burdick, M.F. Reid, Phys. Rev. Lett. 71 (1993) 3892.
[13] G.W. Burdick, C.K. Jayasankar, F.S. Richardson, M.F. Reid, Phys. Rev. B 50 (1994) 16309.
[14] D.J. Newman, B. Ng, Rep. Prog. Phys. 50 (1989) 699.
[15] V. Hurtubise, K.F. Freed, Adv. Chem. Phys. 83 (1993) 465.
[16] B.H. Brandow, in: B.R. Barrett (Ed.), Effective Interactions and Operators in Nuclei, vol. 40 of Lecture Notes in Physics, Springer, 1975, pp. 1–24.
[17] I. Lindgren, J. Morrison, Atomic Many-Body Theory, 2nd ed., Springer-Verlag, Berlin, 1982.
[18] D.J. Newman, Adv. Phys. 20 (1971) 197.
[19] Q. Wang, G.E. Stedman, J. Phys. B: At. Mol. Opt. Phys. 26 (1993) 1415.