Calculation of single-beam two-photon absorption transition rate of rare-earth ions using effective operator and diagrammatic representation

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Abstract

Effective operators needed in single-beam two-photon transition calculations have been represented with modified Goldstone diagrams similar to the type suggested by Duan and co-workers [J. Chem. Phys. 121, 5071 (2004)]. The rules to evaluate these diagrams are different from those for effective Hamiltonian and one-photon transition operators. It is verified that the perturbation terms considered contain only connected diagrams and the evaluation rules are simplified and given explicitly.

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I. INTRODUCTION

Two-photon laser spectroscopy has been used as an important complementary technique in studying optical materials containing lanthanide ions. A recent short review can be found in Ref. 1. Two-photon excitation in a conventional microscope studying biological samples provides great advantages, including low photo-damage and depth discrimination, reduced photobleaching, good separation of the excitation light from the fluorescence emission. Two-photon lasers could give rise to entangled twin beams which offer potential for novel future applications.3 A theoretical challenge in the field of two-photon spectroscopy is prediction of two-photon transition rates.1 4 5

Our work focuses on the calculation of single-beam two-photon absorption rates, particular for optical materials with lanthanides ions. In a former paper,6 we have presented the effective operator method and given a perturbation expansion. In this paper we show that the perturbation expansion can be represented with a kind of diagrams, which can be calculated using one and two-particle matrix elements of interactions and single-particle energies. In Section II, we show how to derive the diagrams from the perturbation expansion; Section III presents those diagrams with only valence internal lines and unusual energy denominators; In Section IV we show the cancellation of disconnected diagrams.

II. CONSTRUCTION OF DIAGRAMS FROM PERTURBATION EXPANSIONS

The calculation of two-photon transition rates has been reduced to the calculation of an effective transition operator.6 The square modulus of the matrix element of the effective operator between two eigenstates of the effective Hamiltonian (usually approximated with semi-classical phenomenological Hamiltonian) is the two-photon transition line strength that can be compared to measurements. In Ref. 6, the effective operator is partitioned into two terms. The first term is calculated with “direct method”5, 6, and the second term is calculated using many-body perturbation theory. It has been shown Ref. 5 that this method contains more general contributions than previous methods. Here we start from that expansion for the second term and consider the usual case where the model space \( P_{I0} \) and \( P_{F0} \) are the same complete model space, denoted as \( P_0 \). By “complete model space” we mean that the model space contains all the bases that can be formed by distributing
the valence electrons among the valence single particle states. Denoting the space orthogonal to $P_0$ by $Q_0$, the perturbative expansion is simplified into the following form

$$
\langle f | T_{\text{eff},0}^2 | i \rangle = \frac{\langle f | O | k \rangle \langle k | O | i \rangle}{(E_f + E_{i0})/2 - E_{k0}} 
$$  \hspace{1cm} (1)

$$
\langle f | T_{\text{eff},1}^2 | i \rangle = \frac{\langle f | V | k_1 \rangle \langle k_1 | O | k_2 \rangle \langle k_2 | O | i \rangle}{(E_{f0} - E_{k10})[E_{f0} + E_{i0}]/2 - E_{k20}]}
$$  \hspace{1cm} (2)

$$
+ \frac{\langle f | O | k_1 \rangle \langle k_1 | O | k_2 \rangle \langle k_2 | V | i \rangle}{[E_{f0} + E_{i0}]/2 - E_{k10}] (E_{i0} - E_{k20})}
$$  \hspace{1cm} (3)

$$
+ \frac{\langle f | O | l \rangle \langle l | V | k \rangle \langle k | O | i \rangle}{(E_{k0} - E_{i0})[E_{f0} + E_{i0}]/2 - E_{k0}}
$$  \hspace{1cm} (4)

$$
+ \frac{\langle f | O | k \rangle \langle k | V | l \rangle \langle l | O | i \rangle}{(E_{k0} - E_{i0})[E_{f0} + E_{i0}]/2 - E_{k0}}
$$  \hspace{1cm} (5)

$$
+ \frac{\langle f | O | k_1 \rangle \langle k_1 | V | k_2 \rangle \langle k_2 | O | i \rangle}{[E_{f0} + E_{i0}]/2 - E_{k10}] [E_{f0} + E_{i0}]/2 - E_{k20}]}
$$  \hspace{1cm} (6)

$$
- \frac{1}{2} \frac{\langle f | V | l \rangle \langle l | O | k \rangle \langle k | O | i \rangle}{[E_{f0} + E_{i0}]/2 - E_{k0}] [E_{f0} + E_{i0}]/2 - E_{k0}]}
$$  \hspace{1cm} (7)

$$
- \frac{1}{2} \frac{\langle f | O | k \rangle \langle k | O | l \rangle \langle l | V | i \rangle}{[E_{f0} + E_{i0}]/2 - E_{k0}] [E_{f0} + E_{i0}]/2 - E_{k0}]}
$$  \hspace{1cm} (8)

where $T_{\text{eff},i}^2$ is the part of effective operator zeroth ($i = 0$) and first order ($i = 1$) in $V$, $k$, $k_1$ and $k_2$ sum over many-particle orthonormal eigenstates of $H_0$ in $Q_0$ and $l$ sums over eigenstates of $H_0$ in $P_0$. $f$ and $i$ are orthonormal eigenstates of $H_0$ in $P_0$.

The perturbation $V$ contains both a one-body operator, denoted as $V_1$ and a two-body operator, denoted as $V_2$. Usually the operator $O$ is one-body operator. Using algebraic representation and corresponding diagrammatic representation given in Ref. 9, Eq. 1 and Eq. 4, $O$, $V_1$ and $V_2$ can be represented by 4, 4 and 9 diagrams respectively. Compositions of two $O$’s and one $V_1$ or $V_2$, as given in Eq. 2 with all possible contractions and all possible relative positions, result into hundreds of diagrams. This prompts us to adapt the modified diagrams given in Ref. 8 to combine the set of diagrams with the same set of vertices, line directions and contractions but different relative position and internal orbit types into one diagram.

A. Adapted connected diagrams with vertices $V_1$ and two $O$

There are altogether 3 ingoing and 3 outgoing lines, with at least 2 pairs of them contracted to form connected diagrams. Therefore the connected diagram can only be zero-body
(a constant) or one-body diagrams. A constant will not contribute to any transition, which is neglected throughout of this paper.

There are three modified one-body diagrams as shown in Fig. 1. Similar to the the case for effective one-photon transition operators in Fig. 4 of Ref. 9, each diagram actually represents contributions from several different terms in Eq. 2 and Eq. 8. For example Fig. 1(a), with different internal line types, includes contributions from Eq. 2, Eq. 3, and Eq. 6. Note that the energy denominator rules will be slightly different from those for effective one-photon transition operators in Ref. 9.

**B. Adapted connected diagram with vertices \( V_2 \) and two \( O \)**

There are altogether 4 ingoing and 4 outgoing lines for for one \( V_2 \) and two \( O \). Therefore connected diagrams can be zero-body, one-body and two-body.

There are also three modified one-body diagrams as shown in Fig. 2, and five modified two-body diagrams as shown in Fig. 3 where two diagrams complex conjugate to Fig. 3(b) and (c) are not given explicitly.

Similar to connected diagrams in Fig. 1, Fig. 2(a), includes contributions from Eq. 2, 3, 4. These contributions form altogether 6 different normal diagrams. Note that the energy denominator rules for contributions from different terms are slightly different.

**C. Rules to evaluate these diagrams**

Remembering that each modified diagram actually represents a set of diagrams with different ordering of vertices and different types of internal lines, it is not difficult to obtain the analytic expressions for these diagrams. For each diagram with fixed vertex ordering, the expression can be calculated by the same rules 1)–7) given in Sec. II, Ref. [10], except that the rule to calculate energy denominators in rule 6) should be modified as follows: Denoting the net outflow energy of a loop enclosing vertices 1, 2, \( \cdots \), \( i \) as

\[
E_{\text{noe}}(1, 2, \cdots, i) = E_{\text{noe}}(1) + E_{\text{noe}}(2) + \cdots + E_{\text{noe}}(i),
\]  

(9)
and supposing the number of $O$ in the loop is $i_O$ ($i_O = 0$, 1, 2) and the number of vertices for the diagram is $n$, the energy denominator can be written as

$$D = \prod_{i=1}^{n-1} \left( \frac{i_O}{2} E_{\text{noe}}(1, 2, \cdots, n) - E_{\text{noe}}(1, 2, \cdots, i) \right).$$  \hspace{1cm} (10)$$

III. DIAGRAMS WITH VERTEX OPERATORS ACTING ONLY ON MODEL SPACES $P_0$

Eq. 4, 5 7 and 8 give diagrams with some vertices, whose bra states and ket states are in model spaces $P_0$. As an example, Eq. 4 have the same operator sequence $OVO$ as that of Eq. 6 but different denominators. They will give diagrams with different evaluation rules, similar to but not exactly the same as those terms in effective Hamiltonian that give folded diagrams. Instead of introducing new folded diagrams, we combine these contributions to the diagrams given above. The rules to evaluate these contributions differ from standard rules in an overall factor $-1/2$ for diagrams from Eq.7 and Eq.8 and in energy denominators by using rules given in Eq.4, Eq.5, Eq.7 and Eq.8.

IV. CANCELLATION OF DISCONNECTED DIAGRAMS

For modified disconnected diagrams with one $V$ vertex and two $O$ vertices, there must be a connected part with only one vertex, which is either $V$ or $O$.

Case A: $V$ is disconnected from other parts. In this case both the ingoing and the outgoing lines of $V$ are valence lines. Such a diagram includes contributions from Eq.6 8 with the same matrix elements but different coefficients due to different energy denominators. Suppose the net-outgoing-energies from the first $O$ and the second $O$ vertices are $\Delta E_1$ and $\Delta E_2$ respectively, and that from the $V$ is $\Delta E_3$. The three different coefficients for the three contributions from Eq.6 8 respectively, are as follows

$$\frac{1}{(\frac{\Delta E_1 + \Delta E_3 + \Delta E_2}{2})^2 - (\Delta E_2 + \Delta E_3)[(\frac{\Delta E_1 + \Delta E_3 + \Delta E_2}{2})^2 - \Delta E_2]} + \left( -\frac{1}{2} \right) \frac{1}{[\frac{(\Delta E_1 + \Delta E_3 + \Delta E_2)^2}{2} - (\Delta E_3 + \Delta E_2)[(\frac{\Delta E_1 + \Delta E_3}{2})^2 - \Delta E_2]} + \left( -\frac{1}{2} \right) \frac{1}{[\frac{(\Delta E_1 + \Delta E_2 + \Delta E_3)^2}{2} - (\Delta E_2 + \Delta E_3)[(\frac{\Delta E_1 + \Delta E_2 + \Delta E_3}{2})^2 - (\Delta E_2 + \Delta E_3)]]} \hspace{1cm} (11)$$

$$\hspace{1cm} (12)$$

$$\hspace{1cm} (13)$$
Case B: one O is disconnected from other parts. Such a diagram includes contributions from Eq. 2–5. It can be verified in the same way as above that all these contributions cancel.

V. CONCLUSION

Diagrams for two-photon transitions rates have been constructed and have been shown to be connected. Simplified one-photon diagrams given in J. Chem. Phys. 121, 5071 (2004) have been adapted to two-photon cases. The algebraic expressions suitable for a general two-photon calculation can be given from these diagrams.

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[1] C.-K. Duan, M. F. Reid, and G. W. Burdick, Phys. Rev. B 66, 155108 (2002).
[2] M. D. Cahalan, I. Parker, S. H. Wei, and M. J. Miller, Nature Reviews Immunology 2, 872 (2002).
[3] B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. Mccord-Maughon, et al., Nature 398, 51 (1999).
[4] M. C. Downer, in Chapter 2 of Laser Spectroscopy of Solids II, edited by W. M. Yen (Springer-Verlag, 1989), chap. 2.
[5] G. W. Burdick, M. F. Reid, C.-K. Duan, J. Chong, and A. Burdick, The puzzle of two-photon rare earth spectra in solids · · · solved? – for dpc ’03, new zeland (2003), presented on International Conference on Dynamical Processes of Excited States in Solids, Christchurch, New Zealand.
[6] C.-K. Duan, G. Ruan, and M. F. Reid, J. Chem. Phys. 121, 8183 (2004).
[7] C.-K. Duan and M. F. Reid, J. Chem. Phys 115, 8279 (2001).
[8] I. Lindgren, Phys. Scr. 32, 611 (1974).
[9] C.-K. Duan, G. Ruan, and M. F. Reid, J. Chem. Phys 121, 5071 (2004).
[10] C.-K. Duan, G. Ruan, and M. F. Reid, J. Chem. Phys 121, 5076 (2004).

[11] B. H. Brandow, Rev. Mod. Phys. 39, 771 (1967).

[12] I. Lindgren, Physica Scripta 32, 291 (1985).

[13] T. T. S. Kuo and E. Osnes, Folded-Diagram Theory of the Effective Interaction in Nuclei, Atoms and Molecules, Vol. 364 of Lecture Notes in Physics (Springer-Verlag, 1990).

Figures
FIG. 1: Modified one-body diagrams first order in $V_1$ for one-beam two-photon transition moment. Note that: 1) the internal lines can be both particle lines and core lines, and the relative altitudes of two $O$’s and $V_1$ change accordingly; 2) contributions of (b) and (c) to the effective operator are complex conjugation of each other.
FIG. 2: Modified one-body diagrams first order in $V_2$ for one-beam two-photon transition moment. Note that: 1) the internal lines can be both particle lines and core lines, and the relative altitudes of two $O$’s and $V_1$ change accordingly; 2) there are natural constrains over several internal lines forming a close loop, since particle lines go upward and core lines go downward, for example, in (b), \{j, k\} must be one particle line and one hole line; 3) contributions of (b) and (c) to the effective operator are complex conjugation of each other.
FIG. 3: Modified two-body diagrams first order in $V_2$ for one-beam two-photon transition moment. Note that: 1) the internal lines can be both particle lines and core lines, and the relative altitudes of two $O$'s and $V_1$ change accordingly; 2) two diagrams with contributions complex conjugate to these of (b) and (c) are not shown here.