Calculation of single-beam two-photon absorption rate of lanthanides: effective operator method and perturbative expansion

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Abstract

Perturbative contributions to single-beam two-photon transition rates may be divided into two types. The first, involving low-energy intermediate states, require a high-order perturbation treatment, or an exact diagonalization. The other, involving high energy intermediate states, only require a low-order perturbation treatment. We show how to partition the effective transition operator into two terms, corresponding to these two types, in such a way that a many-body perturbation expansion may be generated that obeys the linked cluster theorem and has a simple diagrammatic representation.
I. INTRODUCTION

Two-photon laser spectroscopy is an important complementary technique to linear spectroscopy because it has a different parity selection rule, allows access to higher energy states, and has a greater variety of possible polarization choices than linear spectroscopy. The calculation of two-photon absorption for strongly correlated many-electron systems, especially for rare earth ions in solids, dated back to Axe’s work in 1964. However, few quantitative measurements of two-photon absorption were made until the early 1980’s. Extensive measurements have been carried out thereafter. Most of these measurements cannot be explained by Axe’s lowest-order calculations, and as a result, many calculations, some using perturbation theory and some using full calculations in truncated spaces, have been carried out to interpret the experimental results. Recently, we have been able to explain the puzzling two-photon absorption intensities and polarization dependences of Gd$^{3+}$:LaF$_3$ and Eu$^{2+}$:CaF$_2$ by full calculations in a truncated $4f^N + 4f^{N-1}d$ space. However, these calculations cannot explain the two-photon absorption intensities of Sm$^{3+}$, Eu$^{3+}$ and Tb$^{3+}$ doped in elpasolites. It appears that contributions from high-order perturbations or high energy intermediate states must be considered.

A systematic way to calculate properties of many-body systems is using effective Hamiltonians and operators. These techniques have been extensively developed in the literature. The basic idea is to transform the exact time-independent (usually many-body) Hamiltonian $H$ into an effective Hamiltonian $H_{\text{eff}}$ acting on a restricted model space of manageable dimension. The exact eigenvalues and model space eigenvectors (not the exact eigenvectors) can be obtained by diagonalizing $H_{\text{eff}}$. For a time-independent operator $O$, such as a transition moment operator, an effective operator $O_{\text{eff}}$ may be introduced that gives the same matrix elements between the model space eigenvectors of $H_{\text{eff}}$ as those of the original operator $O$ between the corresponding true eigenvectors of $H$. Although the forms of $H_{\text{eff}}$ and $O_{\text{eff}}$ are generally more complicated than, respectively, $H$ and $O$, the calculations based on $H_{\text{eff}}$ and $O_{\text{eff}}$ have many advantages over variational and other direct calculations based on $H$ and $O$, such as smaller bases, less calculation effort, order by order approximations, and the calculation of all eigenvalues and transition matrix elements simultaneously for a multi-dimensional model space. More details on effective operators can be found in a recent paper of Duan and Reid and references therein.
Many-body perturbation theory (MBPT) may be used to expand effective Hamiltonians and operators order by order. The calculations are often represented by Goldstone diagrams.\textsuperscript{31,32} The linked cluster theorem\textsuperscript{25,32,33} implies that disconnected diagrams cancel for effective Hamiltonians and effective operators, provided that the model space has been carefully chosen and the model states have been properly orthogonalized. This cancellation reduces the number of high order diagrams greatly and ensures size consistency. The linked cluster theorem also holds for one-photon transition operators.\textsuperscript{25,29} However, the application of MBPT to two-photon transitions is more difficult than the case of one-photon transitions, in that there are energy denominators in two-photon transition operators that contain both the photon energies and exact electronic energies.\textsuperscript{17,34} Also, the intermediate states can be any eigenstates of the system, including states in the model spaces containing initial and final states and other low excited states, making the energy denominators change drastically and makes perturbative expansions for these intermediate states impossible.

In this paper, we explore the effective operator method for two-photon transition calculations by combining exact calculations in a truncated space\textsuperscript{18,19} with perturbative methods for the rest of the states.\textsuperscript{17,34} In section II we review the basic formalism for effective operator methods; In section III the partition of two-photon transition operator is given in detail; Section IV presents the perturbation expansion that may be suitable for diagram representation and applying linked cluster theorem. The diagram representation and diagram evaluation rules and linked cluster theorem themselves for effective two-photon transition operator are highly nontrivial and will be presented in a followed paper.

II. BASIC FORMALISM

Most of the formalism required has been treated in detail in a monograph by Lindgren and Morrison\textsuperscript{32} and more recently summarized by Killingbeck and Jolicard.\textsuperscript{30} The concept of biorthogonal model space eigenvectors has been summarized by Duan and Reid.\textsuperscript{29} Here shall only give a brief description of the formalism necessarily in the presentation that follows.

The time-independent Hamiltonian $H$ is written as the sum of a model Hamiltonian $H_0$ and a perturbation $V$

$$H = H_0 + V.$$  \hspace{1cm} (1)

Usually $H_0$ is chosen in such a way that its eigenvalues and eigenvectors can be obtained
more easily than for $H$. For example, when $H$ is the Hamiltonian for a many-body system, $H_0$ is usually chosen such that each particle moves independently in the average field of other particles and $V$ denotes the remainder of $H$.

A complete set of orthonormal eigenvectors $\{\ket{\alpha}\}$ and corresponding eigenvalues $\{E_0^\alpha\}$ for $H_0$ are assumed to be available

$$H_0\ket{\alpha} = E_0^\alpha \ket{\alpha}, \quad (2)$$
$$\langle \alpha|\beta \rangle = \delta_{\alpha\beta}. \quad (3)$$

A general model space $P_0$, often referred to as a quasi-degenerate model space, is defined as the space spanned by $d$ successive eigenvectors of $H_0$ (not necessarily strictly degenerate). The remaining part of the Hilbert space is called the orthogonal space $Q_0$. Here we denote the associated projection operators also as $P_0$ and $Q_0$:

$$P_0 = \sum_{\alpha=1}^{d} \ket{\alpha}\bra{\alpha}, \quad (4)$$
$$Q_0 = \sum_{\alpha>d} \ket{\alpha}\bra{\alpha} = 1 - P_0 \quad (5)$$

It has been shown that $d$ eigenvectors of the full Hamiltonian $\ket{\Psi^\alpha} (\alpha = 1, \ldots, d)$ can usually be projected into the model space as $d$ linearly independent functions $\ket{\Psi_0^\alpha}$ in $P_0$. The wave operator $\Omega_P$ is defined as an operator that transforms all the $d$ model functions back into the corresponding exact eigenvectors.

$$\ket{\Psi_0^\alpha} = P_0 \ket{\Psi^\alpha} \quad (6)$$
$$\ket{\Psi^\alpha} = \Omega_P \ket{\Psi_0^\alpha}. \quad (7)$$

Note that $\ket{\Psi_0^\alpha}$s are not necessarily eigenstates of $H_0$, but a linear combination of those eigenstates of $H_0$ in $P_0$. We shall call the space spanned by the $d$ exact eigenvectors $P$. The wave operator $\Omega_P$ satisfied the ordinary Bloch equation:

$$[\Omega_P, H_0] = (V\Omega_P - \Omega_PP_0V\Omega_P)P_0. \quad (8)$$

Usually the $\ket{\Psi_0^\alpha}$ are not orthogonal but are chosen to be normalized to unity. As a consequence $\ket{\Psi^\alpha}$ is not normalized to unity. Denote

$$\langle \Psi^\alpha|\Psi^\beta \rangle = N_0^2\delta_{\alpha\beta}. \quad (9)$$
An effective Hamiltonian \( H_{\text{eff}} \) acting on the model space, which gives the \( d \) exact eigenvalues and model eigenvectors upon diagonalizing, can now be defined. Its form and eigen-equation are

\[
H_{\text{eff}} = P_0 H \Omega_P P_0 = P_0 H_0 P_0 + P_0 V \Omega_P P_0, \tag{10}
\]

\[
H_{\text{eff}} |\Psi_0^\alpha\rangle_k = E^\alpha |\Psi_0^\alpha\rangle_k. \tag{11}
\]

Instead of calculating \( \Omega_P \) directly from (8), the effective Hamiltonian are usually calculated via perturbation theory or phenomenological method and then diagonalized to give eigenvalues \( E^\alpha \) and eigenvectors \( |\Psi_0^\alpha\rangle_k \). It is straightforward to find from a set of vectors \( b(\Psi_0^\alpha) \) in the model space such that

\[
b(\Psi_0^\alpha | \Psi_0^\beta) = \delta_{\alpha\beta} \tag{12}
\]

\[
|\Psi_0^\alpha\rangle_k b(\Psi_0^\beta) = P_0 \tag{13}
\]

It is straightforward to show that

\[
b(\Psi_0^\alpha | (\Omega_P^+ \Omega_P)^{-1} \in P_0, \tag{14}
\]

\[
b(\Psi_0^\alpha | (\Omega_P^+ \Omega_P)^{-1} \Omega_P^+ \Omega_P |\Psi_0^\beta) = \delta_{\alpha\beta}, \tag{15}
\]

\[
b(\Psi_0^\alpha | H_{\text{eff}} = E^\alpha b(\Psi_0^\alpha) \tag{16}
\]

which together with Eq. (7) and Eq. (9) show that

\[
b(\Psi_0^\alpha | (\Omega_P^+ \Omega_P)^{-1} \Omega_P^+ = N_{\alpha}^{-2} \langle \Psi_0^\alpha | \tag{17}
\]

\[
P = \sum_{\alpha} \Omega_P P_0 (\Omega_P^+ \Omega_P)^{-1} \Omega_P^+. \tag{18}
\]

The transition matrix element of an operator \( O \) between states \( \langle \Psi^\alpha | (\alpha \in A) \) and \( \langle \Psi^\beta | (\beta \in B) \) is

\[
O_{\alpha\beta} = \frac{\langle \Psi^\alpha | O | \Psi^\beta \rangle}{N_\alpha N_\beta}. \tag{19}
\]

Defining

\[
O_{\text{eff}} = (\Omega_P^+ \Omega_P)^{-1} \Omega_P^+ O \Omega_P, \tag{20}
\]

it can be shown that

\[
b(\Psi_0^\alpha | O_{\text{eff}} | \Psi_0^\beta) = \frac{N_\beta}{N_\alpha} O_{\alpha\beta}, \tag{21}
\]

\[
O_{\alpha\beta} = (b(\Psi_0^\alpha | O_{\text{eff}} | \Psi_0^\beta) b(\Psi_0^\beta | O_{\text{eff}} | \Psi_0^\alpha)^* )^{-1/2}. \tag{22}
\]
III. PARTITION OF EFFECTIVE TRANSITION OPERATORS FOR SINGLE BEAM TWO-PHOTON ABSORPTION

The perturbative expansion of a general two-beam two-photon transition rate has been discussed by Duan and Reid\textsuperscript{[34]}. Here we develop the perturbative expansion specialized for the single-beam case. We will see that the calculation can be greatly simplified.

The line strength is proportional to the square modulus of following expression

\[ T_{fi} = \frac{\langle f|O|k\rangle\langle k|O|i\rangle}{E_i + \omega - E_k} \]

(23)

\[ = \langle f|O\frac{1}{(E_f + E_i)/2 - H}O|i\rangle. \]

(24)

where \(|f\rangle (f \in F), |i\rangle (i \in I)\) and \(|k\rangle (k \in F \cup I \cup K)\) are normalized exact eigenstates of the systems, \(E_f, E_i, E_k\) are the corresponding exact eigenvalues, \(F, I\) are the set of final and initial states of the transition. \(K\) is the set of states of the system not included in \(I\) and \(F\). The intermediate eigenstates \(k\) can be any eigenstates of the system, including eigenstates in the sets of initial and final states. The calculation of \(T_{fi}\) can be divided into two terms, a term \(T_1\) with “small” denominators, where \(k \in I \cup F\), and a term \(T_2\) with “large” denominators, where \(k \in K\). The operator can be formally written as

\[ T = T^1 + T^2 \]

(25)

\[ T^1 = \sum_{f,i} |f\rangle\langle i| \sum_{k \in I \cup F} \frac{O_{fk}O_{ki}}{(E_f + E_i)/2 - E_k} \]

(26)

\[ = O\frac{P_{I \cup F}}{(H^F + H^I)/2 - H}O \]

(27)

\[ T^2 = \sum_{f,i} |f\rangle\langle i| \sum_{k \in I \cup F} \frac{O_{fk}O_{ki}}{(E_f + E_i)/2 - E_k} \]

(28)

\[ = O\frac{P_{K}}{(H^I + H^F)/2 - H}O. \]

(29)

Note that \(H^F\) and \(H^I\) are actually acting on the transition final (on the leftmost) and initial states (on the rightmost) and the equalities in (27) and (29) above are for notational convenience.

The effective operator for \(T^1\) is

\[ T^1_{\text{eff}} = \sum_{f,i} |\Psi_0^f\rangle_k b\langle \Psi_0^i| \sum_{m \in F \cup I} \frac{b\langle \Psi_0^f|O_{\text{eff}}|\Psi_0^m\rangle_k b\langle \Psi_0^m|O_{\text{eff}}|\Psi_0^i\rangle_k}{(E_f + E_i)/2 - E_m}. \]

(30)
Note that in this expression we use the exact eigenvalues and model space eigenvectors. The matrix elements of the effective operators are between states in spaces $P_{F0}$ and $P_{I0}$ (which may be the same). The matrix elements may be calculated from the effective Hamiltonian $H_{\text{eff}}$ and effective operator $O_{\text{eff}}$.

The effective operator for $T^2$ can be formally written as

$$T^2_{\text{eff}} = (\Omega^+_F\Omega_F)^{-1}\Omega^+_F\Omega_K P^0_K (H^F_{\text{eff}} + H^I_{\text{eff}})/2 - H^K_{\text{eff}} P^0_K (\Omega^+_K\Omega_K)^{-1}\Omega^+_K\Omega_I.$$  

(31)

Once again, $H^F_{\text{eff}}$ and $H^I_{\text{eff}}$ act on the bra and ket model space respectively.

The space $K$ includes all other states of the system than those limited number of states in $I$ and $F$. It is usually of infinite dimension and the calculation of $H^K_{\text{eff}}, O_{\text{eff}}(F,K)$ and $O_{\text{eff}}(K,I)$ is usually impractical or at least very tedious. Perturbative expansions giving in the following section can be used to calculate $T^2_{\text{eff}}$ by an order-by-order approximation.

IV. PERTURBATIVE EXPANSION

Perturbative expansions of $H_{\text{eff}}$ and $O_{\text{eff}}$ have been discussed in, for example, Refs. 32 and 29 by applying the Bloch equation iteratively. Here we expand $T^2_{\text{eff}}$ by perturbation theory to avoid direct calculation of $H_{\text{eff}}$ and $O_{\text{eff}}$ in model space $K$, which is usually of infinite dimension.

Defining

$$S = 1/[(H^F_0 + H^I_0)/2 - H^K_0],$$  

(32)

$$\Delta V = V^K_{\text{eff}} - \frac{1}{2}(V^F_{\text{eff}} + V^I_{\text{eff}}),$$  

(33)

where

$$V^\xi_{\text{eff}} = P_{\xi0} V^\xi_0 P_{\xi0}$$  

(34)

$$H^\xi_0 = P_{\xi0} H_0 P_{\xi0}$$  

(35)

act on the transition initial, final and intermediate states for $\xi = I, F, K$ respectively. The energy denominator can be expanded as follows

$$\frac{1}{(H^F_{\text{eff}} + H^I_{\text{eff}})/2 - H^K_{\text{eff}}} = S \sum_{n=0}^{\infty} (\Delta V S)^n$$  

(36)

$$= S + S V^K_{\text{eff}} S - \frac{1}{2} V^F_{\text{eff}} S^2 - \frac{1}{2} S^2 V^I_{\text{eff}} + \ldots$$  

(37)
Using the Bloch equation, $\Omega_K$ can be expanded as follows

$$\Omega_K = P_{K_0} + R_K (V \Omega_K - \Omega_K V)$$

$$= P_{K_0} + R_K V P_{K_0} + R_K V R_K V P_{K_0} - R^2 V P_{K_0} P_{K_0},$$

where

$$R_K = \frac{P_{(I \cup F)0}}{H_0^K - H_0^{I \cup F}}.$$

Using the above expressions, the matrix elements of the zeroth and first-order of $T^2_{\text{eff}}$ between eigenstates of $H_0$, $|f\rangle$ ($f \in P_{F_0}$) and $|i\rangle$ ($i \in P_{I_0}$) are:

$$\langle f | T^2_{\text{eff},0} | i \rangle = \sum_{k \in P_{K_0}} \frac{\langle f | O | k \rangle \langle k | O | i \rangle}{(E_{f0} + E_{i0})/2 - E_{k0}}$$

$$\langle f | T^2_{\text{eff},1} | i \rangle = \left\{ \sum_{k \in P_{K_0}} \left[ \sum_{l \in Q_{F_0}} \frac{\langle f | V | l \rangle \langle l | O | k \rangle \langle k | O | i \rangle}{(E_{f0} - E_{i0})[(E_{f0} + E_{i0})/2 - E_{k0}]} \right. \right.$$

$$+ \sum_{l \in Q_{F_0}} \frac{\langle f | O | k \rangle \langle k | O | l \rangle \langle l | V | i \rangle}{(E_{i0} - E_{f0})[(E_{f0} + E_{i0})/2 - E_{k0}]} \right.$$

$$+ \sum_{l \in Q_{I_0}} \sum_{k \in P_{K_0}} \left[ \frac{\langle f | O | k \rangle \langle k | V | l \rangle \langle l | O | i \rangle}{(E_{k0} - E_{i0})[(E_{f0} + E_{i0})/2 - E_{k0}]} + \frac{\langle f | O | k \rangle \langle k | V | l \rangle \langle l | O | i \rangle}{(E_{k0} - E_{i0})[(E_{f0} + E_{i0})/2 - E_{k0}]} \right]$$

$$+ \sum_{k_1 \in P_{K_0}} \sum_{k_2 \in P_{K_0}} \frac{\langle f | O | k \rangle \langle k_1 | V | k_2 \rangle \langle k_2 | O | i \rangle}{(E_{f0} + E_{i0})/2 - E_{k_10}][E_{f0} + E_{i0})/2 - E_{k_20}]$$

$$- \frac{1}{2} \sum_{f' \in P_{F_0}} \sum_{k \in P_{K_0}} \frac{\langle f | V | f' \rangle \langle f' | O | k \rangle \langle k | O | i \rangle}{(E_{f0} + E_{i0})/2 - E_{k0}][E_{f'0} + E_{i0})/2 - E_{k0}]$$

$$- \frac{1}{2} \sum_{i' \in P_{I_0}} \sum_{k \in P_{K_0}} \frac{\langle f | O | k \rangle \langle k | O | i' \rangle \langle i' | V | i \rangle}{(E_{f0} + E_{i0})/2 - E_{k0}][E_{f0} + E_{i0})/2 - E_{k0}]} \right\}$$

where all eigenvectors and energies are for model Hamiltonian $H_0$ and matrix elements are between eigenvectors of $H_0$. The transition rates can then be calculated straightforwardly from Eq.22 since the model space eigenvectors are assumed to have already been calculated from Eq.11.

Terms of second order or higher in $V$ can also be obtained straightforwardly. There are about 20 second order terms but around 100 third order terms. Fortunately, with a suitable partition of $T$ into $T^1$ and $T^2$, usually only the zeroth and first order terms of $T^2$ need to be calculated, except when zeroth and first-order terms become zero due to selection rules. In such cases the number of nonzero second order terms is often greatly reduced.
V. CONCLUSION

A method to calculate single-beam two-photon absorption transition rates for many-electron systems has been developed using effective operator methods together with many-body perturbation theory. In this method the contributions to two-photon transition operator are partitioned into two terms, one with small drastically varying denominators, which is treated by doing an exact calculation in truncated spaces and the other with numerous intermediate states and large energy denominators, which is treated systematically with many-body perturbation theory. Compared to previous methods, the method presented here has the accuracy of full calculation for contributions due to drastic-varying low-energy intermediate states and the simplicity of low-order many-body perturbation theory for contributions due to high energy intermediate states. It is also expected that there are linked diagram representations for the order-by-order expansion.

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