General formula for phonon-assisted n-photon absorption in solids*

Deng Hong-Xiang(邓洪祥)[a], Jiang Xiao-Dong(蒋晓东)[a)b)†], Xiang Xia(向 霞)[a], Sun Kai(孙 凯)[c], Yuan Xiao-Dong(袁晓东)[a)b)], Zheng Wan-Guo(郑万国)[b], Gao Fei(高 飞)[d], and Zu Xiao-Tao(祖小涛)[a)‡]

[a] *Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*

[b] *Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang* 621900, *China*

[c] *Department of Materials Engineering and Sciences, University of Michigan, Ann Arbor, MI* 48109, *USA*

[d] *Pacific Northwest National Laboratory, P. O. Box* 999, *Richland, WA* 99352, *USA*

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A general formula for phonon-assisted n-photon absorption in solids is obtained by $(n+1)$-th order perturbation technique. The complicated calculation process for transition element of n-photon absorption is simply demonstrated by a diagram approach that is proposed in this work. We find that the transition element for the n-photon absorption has a simple form, i.e., it is just the first term of the n-th order fist kind Bessel function.

Keywords: general formula, phonon-assisted photons absorption, n order perturbation technique, diagram approach, intense laser

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1. Introduction

It is well known that an electron in a conduction band of solid cannot absorb photon and conserve energy and momentum without simultaneously absorbing or emitting a phonon, or simultaneously scattering off an impurity in the same band, since the momentum of a photon is very small.[1−7] Phonon-assisted photon absorption can happen in semiconductor material,[3,8] dielectric material,[2,9] and metal material.[10] Therefore, the study of this photon absorption mechanism is of basic significance for solid physics. Moreover, in an intense laser field phonon-assisted photon absorption of conduction band electron (CBE) plays an important role in the laser induced damage (LID) in transparent solids,[2,11−15] which is a still limiting factor in the development of the high power laser systems or optoelectronic devices; and the multi-photon process usually needs to be taken into account.[16]

In quantum mechanics, we need $(n+1)$-th order perturbation technique to calculate the phonon-assisted n-photon absorption (one is for phonon, n for photons). The previous calculations[1−3] are mostly related to phonon-assisted one-photon absorption or two-photon absorption, and no report about the general formula of n-photon absorption is available. One of the reasons is that the calculation of high order perturbation theory is quite complicated and can hardly find the calculation rule for the general cases. With the help of a diagram approach which is demonstrated in this work, we obtain the general formula. Figure 1 is the scheme of phonon-assisted photon absorption process of CBE, where E_i is the initial energy of a CBE; $E_f = E_i + n\hbar\omega \pm \hbar\omega_{\rm p}$ is the final energy of a CBE which has absorbed n photons in the transition process.

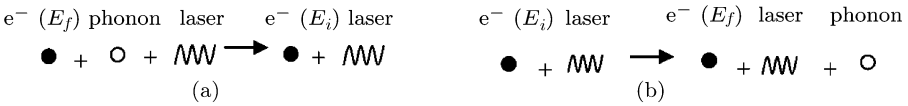


Fig. 1. Schemes of phonon-assisted photon absorption process of CBE, where CBE absorbs a phonon to keep conservations of both energy and momentum in absorption process (a), and CBE emits a phonon to keep conservations of both energy and momentum in absorption process.

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†E-mail: jiangxdong@163.com

‡Corresponding author. E-mail: xtzu@uestc.edu.cn

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2. $(n+1)$-th order perturbation in time-dependent perturbation theory

First, we make a summarization for the n-th order perturbation in time-dependent perturbation theory. If we denote the total Hamiltonian of the system as

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \tag{1}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian in the system and independent of time; $\hat{V}(t)$ is the perturbation Hamiltonian, and the expression for $(n+1)$-th order perturbation can be summarized as (the detailed calculation process can be seen in Appendix)

$$W = \frac{2\pi}{\hbar^2}\left|\sum_{m_1,m_2,\ldots m_n} \frac{\langle f|\hat{V}|m_n\rangle\cdots\langle m_K|\hat{V}|m_{K-1}\rangle\cdots\langle m_2|\hat{V}|m_1\rangle\langle m_1|\hat{V}|i\rangle}{(E_i-E_{m_1})\cdots(E_i-E_K)\cdots(E_i-E_{m_n})}\right|^2 \delta\left(\frac{E_f-E_i}{\hbar}\right) \tag{2}$$

with $|m_1\rangle$, $|m_2\rangle$,..., $|m_n\rangle$ denoting the intermediate states, and $E_{m_1}, E_{m_2},\ldots, E_{m_n}$ referring to the corresponding intermediate energies. The transition element in Eq. (2) can be written as

$$S = \sum_{m_1,m_2,\ldots m_n} \frac{\langle f|\hat{V}|m_n\rangle\cdots\langle m_K|\hat{V}|m_{K-1}\rangle\cdots\langle m_2|\hat{V}|m_1\rangle\langle m_1|\hat{V}|i\rangle}{(E_i-E_{m_1})\cdots(E_i-E_K)\cdots(E_i-E_{m_n})}. \tag{3}$$

3. Phonon assisted photon absorption

In the phonon-assisted photon absorption process, the perturbation Hamiltonian is

$$\hat{V} = \hat{H}_{\rm el} + \hat{H}_{\rm ep}, \tag{4}$$

where $\hat{H}_{\rm el}$ and $\hat{H}_{\rm ep}$ are the electron-light interaction Hamiltonian and the electron–phonon interaction Hamiltonian, respectively. For monochromatic linear polarized laser, $\hat{H}_{\rm el}$ and $\hat{H}_{\rm ep}$ can be written as[1,2,9]

$$\begin{aligned}\hat{H}_{\rm el} &= \frac{e\boldsymbol{A}_0\cos(\boldsymbol{k}_L\cdot\boldsymbol{r}-\omega t)\cdot\hat{\boldsymbol{P}}}{m^*}\\ &= C_{\rm el}\boldsymbol{a}\cdot\hat{\boldsymbol{k}}[{\rm e}^{{\rm i}\boldsymbol{k}_L}b_{\boldsymbol{k}_L}+{\rm e}^{-{\rm i}\boldsymbol{k}_l}b^\dagger_{\boldsymbol{k}_L}],\\ \hat{H}_{\rm ep} &= \sum_{\boldsymbol{q}} C_{\rm ep}({\rm e}^{{\rm i}\boldsymbol{q}\cdot\boldsymbol{r}}b_{\boldsymbol{q}}-{\rm e}^{-{\rm i}\boldsymbol{q}\cdot\boldsymbol{r}}b^\dagger_{\boldsymbol{q}}),\end{aligned} \tag{5}$$

where $\boldsymbol{A}_0$ and ω are the laser vector potential and the laser frequency, respectively; $\boldsymbol{a}$ denotes the unity vector of laser potential; m^* the effective mass of CBE; $\hat{\boldsymbol{P}}$ the quasi-momentum operator of CBE; $\hat{\boldsymbol{k}}$ the wave vector operator of CBE; $\boldsymbol{q}$ the wave vector of phonon; $\boldsymbol{k}_l$ the wave vector of photon; $C_{\rm el}$ and $C_{\rm ep}$ refer to the electron–light and electron–phonon coupling constants, respectively; $b^\dagger_{\boldsymbol{q}}$ and $b_{\boldsymbol{q}}$ the creation and annihilation operators of phonon, respectively; $b^\dagger_{\boldsymbol{k}_l}$ and $b_{\boldsymbol{k}_l}$ the creation and annihilation operators of photon, respectively. The phonon-assisted n-photon absorption rate now can be calculated from Eq. (2).

For simplicity, we will show only the photon absorption process ($n>0$) which is by the help of absorbing a phonon (the calculation process of phonon emission or photon emission ($n<0$) is similar).

3.1. Phonon-assisted one-photon absorption

The momentum of photon is usually neglected in the transition process.[1] Here we make a discussion about this approximation. The change of momentum in the photon absorption process is on the order of $\sqrt{\hbar\omega m^*}$ and the momentum of photon is $\hbar\omega/c$. Comparing $\sqrt{\hbar\omega m^*}$ with $\hbar\omega/c$, we have an expression of $m^*c^2 \gg \hbar\omega$. So it is a good approximation for the usual radiation laser.

For one-photon absorption process, the initial state and the final state can be written as

$$\begin{aligned}|i\rangle &= |\boldsymbol{k}\rangle|m\rangle|n_{\rm p}\rangle = |\boldsymbol{k};m;n_{\rm p}\rangle,\\ |f\rangle &= |\boldsymbol{k}+\boldsymbol{q}\rangle|m-1\rangle|n_{\rm p}-1\rangle\\ &= |\boldsymbol{k}+\boldsymbol{q};m-1;n_{\rm p}-1\rangle,\end{aligned} \tag{6}$$

where $\boldsymbol{k}$ refers to the initial wave vector $\boldsymbol{k}_i$ of CBE; $\boldsymbol{k}+\boldsymbol{q}$ the final wave vector $\boldsymbol{k}_f$ of CBE; m and $m-1$ denote the initial photon number and the final photon number of the laser, respectively; $n_{\rm p}$ and $n_{\rm p}-1$ the initial phonon occupation number in solid and the final phonon number, respectively.

Because the first order transition element $\langle f|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|i\rangle$ is zero, we need to consider the second order

perturbation. The initial and the final energies of the system, respectively, are

$$E_i = E_{\boldsymbol{k}} + m\hbar\omega + n\hbar\omega_{\rm p},$$
$$E_f = E_{\boldsymbol{k}+\boldsymbol{q}} + (m-1)\hbar\omega + (n-1)\hbar\omega_{\rm p}, \quad (7)$$

where $E_{\boldsymbol{k}} = (\hbar k)^2/2m^*$ and $E_{\boldsymbol{k}+\boldsymbol{q}} = [\hbar(k+q)]^2/2m^*$ are kinetic energies of CBE; $\hbar\omega_{\rm p}$ is the energy of phonon. If the phonon is absorbed first, the intermediate energy and the corresponding state are given as

$$E_{m_1} = E_{\boldsymbol{k}+\boldsymbol{q}} + m\hbar\omega + (n_{\rm p}-1)\hbar\omega_{\rm p},$$
$$|m_1\rangle = |\boldsymbol{k}+\boldsymbol{q}; m; n_{\rm p}-1\rangle, \quad (8)$$

and if the photon is absorbed first

$$E_{m_1} = E_{\boldsymbol{k}} + \hbar\omega_{\rm p},$$
$$|m_1\rangle = |\boldsymbol{k}; m-1; n_{\rm p}\rangle. \quad (9)$$

Substituting Eqs. (7)–(9) into Eq. (3), we obtain the transition element for phonon-assisted one-photon absorption

$$S = \frac{\langle f|\hat{H}_{\rm ep}+\hat{H}_{\rm el}|\boldsymbol{k}+\boldsymbol{q}; m; n_{\rm p}-1\rangle\langle n_{\rm p}-1; m; \boldsymbol{k}+\boldsymbol{q}|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|\,i\rangle}{(E_{\boldsymbol{k}}+m\hbar\omega+n_{\rm p}\hbar\omega_{\rm p})-[E_{\boldsymbol{k}+\boldsymbol{q}}+m\hbar\omega+(n_{\rm p}-1)\hbar\omega_{\rm p}]}$$
$$+\frac{\langle f|\hat{H}_{\rm ep}+\hat{H}_{\rm el}|\boldsymbol{k}; m-1; n_{\rm p}\rangle\langle n_{\rm p}; m-1; \boldsymbol{k}|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|i\rangle}{(E_{\boldsymbol{k}}+m\hbar\omega+n_{\rm p}\hbar\omega_{\rm p})-[E_{\boldsymbol{k}}+(m-1)\hbar\omega+n_{\rm p}\hbar\omega_{\rm p}]}+0,$$

only two ways above have the contribution to transition element; for other way

$$\langle f|\hat{H}_{\rm ep}+\hat{H}_{\rm el}|m_1\rangle\langle m_1|\hat{H}_{\rm ep}+\hat{H}_{\rm el}|i\rangle = 0. \quad (10)$$

Since $E_f = E_i$ (energy conservation) in the transition process, we have

$$E_{\boldsymbol{k}+\boldsymbol{q}} = E_{\boldsymbol{k}} + \hbar\omega_{\rm p} + \hbar\omega. \quad (11)$$

Substituting Eq. (11) into Eq. (10), we obtain

$$\begin{aligned} S &= \frac{(C_{\rm ep}\sqrt{n_{\rm p}})C_{\rm el}\sqrt{m}\ (\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a}}{-\hbar\omega m^*} \\ &\quad + \frac{(C_{\rm ep}\sqrt{n_{\rm p}})C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a}}{\hbar\omega m^*} \\ &= -\frac{C_{\rm ep}\sqrt{n_{\rm p}}C_{\rm el}\sqrt{m}\,\boldsymbol{a}\cdot\boldsymbol{q}}{\hbar\omega m^*} \\ &= -\frac{C_{\rm ep}\sqrt{n_{\rm p}}C_{\rm el}\sqrt{m}\,\boldsymbol{a}\cdot(\boldsymbol{k}_f-\boldsymbol{k}_i)}{\hbar\omega m^*}. \end{aligned} \quad (12)$$

Rewriting Eq. (12) in the form of classical electromagnetic field, we have

$$S = -C_{\rm ep}\sqrt{n_{\rm p}}\frac{e\boldsymbol{A}_0\cdot(\boldsymbol{P}_f-\boldsymbol{P}_i)}{2\hbar\omega m^*}. \quad (13)$$

Substituting Eq. (13) into Eq. (2), we obtain the transition rate for all final states of $\boldsymbol{S}_f$

$$\begin{aligned} W &= \frac{2\pi}{\hbar^2}\int|S|^2\delta\left(\frac{E_f-E_i}{\hbar}\right)\mathrm{d}\boldsymbol{S}_f \\ &= \frac{2\pi}{\hbar}\int|S|^2\delta(E_f-E_i)\mathrm{d}\boldsymbol{S}_f, \end{aligned} \quad (14)$$

where the formula of Dirac delta function

$$\int f(x)\delta\left(\frac{x}{a}-\frac{b}{a}\right)\mathrm{d}x = af(b) = a\int f(x)\delta(x-b)\mathrm{d}x$$

has been employed.[1]

3.2. Phonon-assisted two-photon absorption

For two-photon absorption process, the initial state and the final state are

$$|i\rangle = |\boldsymbol{k}; m; n_{\rm p}\rangle,$$
$$|f\rangle = |\boldsymbol{k}+\boldsymbol{q}; m-2; n_{\rm p}-1\rangle, \quad (15)$$

where $\boldsymbol{k}$ denotes the initial wave vector $\boldsymbol{k}_i$ of CBE; $\boldsymbol{k}+\boldsymbol{q}$ the final wave vector $\boldsymbol{k}_f$ of CBE; m and $m-2$ refer to the initial photon number and the final photon number of the laser, respectively; $n_{\rm p}$ and $n_{\rm p}-1$ the initial phonon occupation number in solid and the final phonon number, respectively.

Because the second-order transition element $\langle f|U^{(2)}|i\rangle = 0$, we need to consider the third-order perturbation. The calculation process is similar to the case of one-photon absorption. There are three ways to complete the absorption process from $|i\rangle \to |f\rangle$. These ways can be described as fellows:

(i) CBE first absorbs a phonon, then absorbs one photon, and finally absorbs one photon.

$$|i\rangle \xrightarrow{\bullet} |m_1\rangle \xrightarrow{\circ} |m_2\rangle \xrightarrow{\circ} |f\rangle.$$

Here, symbol "$\bullet$" represents the phonon absorption process, and symbol "$\circ$" denotes the photon absorption process. For this process, we have

$$E_i - E_{m_1} = -2\hbar\omega,$$
$$E_i - E_{m_2} = -\hbar\omega,$$

$$\langle i|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|f\rangle$$
$$=(C_{\rm ep}\sqrt{n_{\rm p}})\left(\frac{C_{\rm el}\sqrt{m}\,(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a}}{m^*}\right)\left(\frac{C_{\rm el}\sqrt{m-1}(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a}}{m^*}\right);$$

the contribution to the transition element from way (i) is

$$S_1=\frac{\langle i|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|f\rangle}{(E_i-E_{m_1})(E_i-E_{m_2})}$$
$$=\frac{(C_{\rm ep}\sqrt{n_{\rm p}})(C_{\rm el}\sqrt{m}\,(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a})(C_{\rm el}\sqrt{m-1}(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a})}{(-2\hbar\omega)\cdot(-1\hbar\omega)\cdot(m^*)^2};\tag{16}$$

(ii) CBE first absorbs a photon, then absorbs one phonon, and finally absorbs one photon.

$$|i\rangle\xrightarrow{\circ}|m_1\rangle\xrightarrow{\bullet}|m_2\rangle\xrightarrow{\circ}|f\rangle.$$

We have

$$E_i-E_{m_1}=\hbar\omega,\quad E_i-E_{m_2}=-\hbar\omega,$$

$$\langle i|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|f\rangle=\left(\frac{C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a}}{m^*}\right)(C_{\rm ep}\sqrt{n_{\rm p}})\left(\frac{C_{\rm el}\sqrt{m-1}(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a}}{m^*}\right).$$

The contribution to the transition element from way (ii) is

$$S_2=\frac{(C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a})(C_{\rm ep}\sqrt{n_{\rm p}})(C_{\rm el}\sqrt{m-1}(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a})}{(\hbar\omega)(-1\hbar\omega)(m^*)^2};\tag{17}$$

(iii) CBE first absorbs one photon, then absorbs one photon, and finally absorbs phonon.

$$|i\rangle\xrightarrow{\circ}|m_1\rangle\xrightarrow{\circ}|m_2\rangle\xrightarrow{\bullet}|f\rangle.$$

In way (iii) $E_i-E_{m_1}=\hbar\omega$, $E_i-E_{m_2}=2\hbar\omega$,

$$\langle i|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|f\rangle=\left(\frac{C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a}}{m^*}\right)\left(\frac{C_{\rm el}\sqrt{m-1}\boldsymbol{k}\cdot\boldsymbol{a}}{m^*}\right)(C_{\rm ep}\sqrt{n_{\rm p}}).$$

The contribution from way (iii) is

$$S_3=\frac{(C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a})(C_{\rm el}\sqrt{m-1}\boldsymbol{k}\cdot\boldsymbol{a})(C_{\rm ep}\sqrt{n_{\rm p}})}{(\hbar\omega)(2\hbar\omega)(m^*)^2}.\tag{18}$$

Substituting Eqs. (16)–(18) in into Eq. (3), we have

$$S=S_1+S_2+S_3+0=\frac{(C_{\rm ep}\sqrt{n_{\rm p}})(C_{\rm el}\sqrt{m}\,(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a})(C_{\rm el}\sqrt{m-1}(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a})}{(-2\hbar\omega)\cdot(-1\hbar\omega)\cdot(m^*)^2}$$
$$+\frac{(C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a})(C_{\rm ep}\sqrt{n_{\rm p}})(C_{\rm el}\sqrt{m-1}(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{a})}{(\hbar\omega)(-1\hbar\omega)(m^*)^2}+\frac{(C_{\rm el}\sqrt{m}\,\boldsymbol{k}\cdot\boldsymbol{a})(C_{\rm el}\sqrt{m-1}\boldsymbol{k}\cdot\boldsymbol{a})(C_{\rm ep}\sqrt{n_{\rm p}})}{(\hbar\omega)(2\hbar\omega)(m^*)^2}+0.$$
$$=\frac{C_{\rm ep}\sqrt{n_{\rm p}}C_{\rm el}\sqrt{m}\,C_{\rm el}\sqrt{m-1}}{(\hbar\omega)^2(m^*)^2}\left(\frac{B^2}{2}-BC+\frac{C^2}{2}\right),$$
$$=C_{\rm ep}\sqrt{n_{\rm p}}\frac{C_{\rm el}\sqrt{m}\,C_{\rm el}\sqrt{m-1}}{(\hbar\omega)^2(m^*)^2}\frac{1}{2}(B-C)^2,\tag{19}$$

where $B=\boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q})=\boldsymbol{a}\cdot\boldsymbol{k}_f$, $C=\boldsymbol{a}\cdot\boldsymbol{k}=\boldsymbol{a}\cdot\boldsymbol{k}_i$, and $C_{\rm ep}\sqrt{n_{\rm p}}\dfrac{C_{\rm el}\sqrt{m}\,C_{\rm el}\sqrt{m-1}}{(\hbar\omega)^2(m^*)^2}$ is the common factor in S_1, S_2, S_3.

Because usually the photon number of light $m\gg1$, we take $\sqrt{m-1}\approx\sqrt{m}\sim A_0$. Then we have

$$S = C_{\rm ep}\sqrt{n_{\rm p}}\frac{1}{2}\left(\frac{e\boldsymbol{A}_0\cdot(\boldsymbol{P}_f-\boldsymbol{P}_i)}{2\hbar\omega m^*}\right)^2. \tag{20}$$

Using Eq. (2), the transition rate for all final states can be written in the same form as that of Eq. (14) as follows:

$$W = \frac{2\pi}{\hbar}\int |S|^2 {\rm d}\boldsymbol{S}_f. \tag{21}$$

To show the laws in the calculation process, we put the three ways together

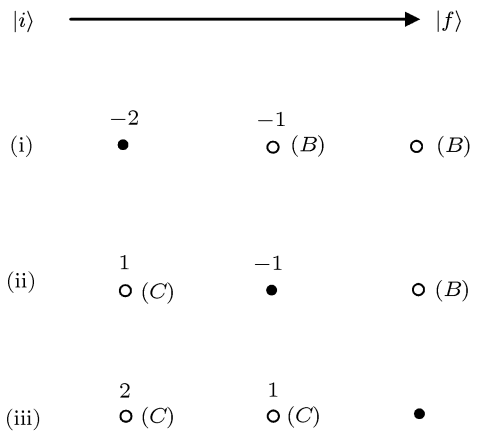


Fig. 2. Diagram for two-photon absorption.

Here, we put the values of $(E_i - E_{m_1})/\hbar$ and $(E_i - E_{m_2})/\hbar$ above • and ∘ in the order of absorption process. In way (i), we put $(E_i - E_{m_1})/\hbar\omega = -2$ and $(E_i - E_{m_2})/\hbar\omega = -1$ above • and ∘ respectively (in way (i), the CBE first absorbs a phonon and then absorbs one photon); in way (ii), the values $(E_i - E_{m_1})/\hbar\omega = 1$ and $(E_i - E_{m_2})/\hbar\omega = -1$ are put above ∘ and • respectively; in way (iii), we put 1 and 2 above ∘ and ∘ respectively.

The value B or C in the brackets represents the wave vector of CBE in photon absorption process, where $B = \boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q})$ and $C = \boldsymbol{a}\cdot\boldsymbol{k}$. In way (i), after the phonon absorption process, the wave vector of CBE becomes $\boldsymbol{k}+\boldsymbol{q}$. So we denote $\circ(B)$ $\circ(B)$ in the right part of symbol "•". In way (ii), the wave vector of CBE is $\boldsymbol{k}$ before phonon absorption process and becomes $\boldsymbol{k}+\boldsymbol{q}$ after phonon absorption. So we denote $\circ(C)$ • $\circ(B)$ in way (ii). In way (iii), the two-photon absorption processes all happen before phonon absorption process; so we have $\circ(C)$ ∘ (C) •. It is easy to find that in the left part of symbol "•" (before phonon absorption process), we have $\circ(C)$; in the right part (after phonon absorption process) of symbol "•", we have $\circ(B)$. For simplicity, the C and the B will not be shown below.

3.3. Phonon-assisted three-photon absorption

There are four ways to complete the absorption process from $|i\rangle \to |f\rangle$. The four ways are as fellows:

(I) $|i\rangle \xrightarrow{\bullet} m_1 \xrightarrow{\circ} m_2 \xrightarrow{\circ} m_3 \xrightarrow{\circ} |f\rangle$;
(II) $|i\rangle \xrightarrow{\circ} m_1 \xrightarrow{\bullet} m_2 \xrightarrow{\circ} m_3 \xrightarrow{\circ} |f\rangle$;
(III) $|i\rangle \xrightarrow{\circ} m_1 \xrightarrow{\circ} m_2 \xrightarrow{\bullet} m_3 \xrightarrow{\circ} |f\rangle$;
(IV) $|i\rangle \xrightarrow{\circ} m_1 \xrightarrow{\circ} m_2 \xrightarrow{\circ} m_3 \xrightarrow{\bullet} |f\rangle$.

For way (I), we have

$$\begin{aligned}
&E_i - E_{m_1} = -3\hbar\omega, \quad E_i - E_{m_2} = -2\hbar\omega, \quad E_i - E_{m_3} = -\hbar\omega;\\
&\langle i|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|f\rangle\\
=\ & C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}(\boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q}))(\boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q}))(\boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q})\\
=\ & C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\left(\frac{1}{m^*}\right)^3 B^3;\\
S_1 =\ & \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\frac{B^3}{(-3)\cdot(-2)\cdot(-1)}.
\end{aligned} \tag{22}$$

For way (II), we have

$$\begin{aligned}
&E_i - E_{m_1} = \hbar\omega, \quad E_i - E_{m_2} = -2\hbar\omega, \quad E_i - E_{m_3} = -\hbar\omega;\\
&\langle i|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el}+\hat{H}_{\rm ep}|f\rangle\\
=\ & C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}(\boldsymbol{a}\cdot(\boldsymbol{k}))(\boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q}))(\boldsymbol{a}\cdot(\boldsymbol{k}+\boldsymbol{q}))\\
=\ & C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\left(\frac{1}{m^*}\right)^3 CB^2,\\
S_2 =\ & \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\frac{B^2C}{1\cdot(-2)\cdot(-1)}.
\end{aligned} \tag{23}$$

For way (III)

$$E_i - E_{m_1} = \hbar\omega, \quad E_i - E_{m_2} = 2\hbar\omega, \quad E_i - E_{m_3} = -1\hbar\omega,$$

$$\begin{aligned}
&\langle i|\hat{H}_{\rm el} + \hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el} + \hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el} + \hat{H}_{\rm ep}|f\rangle \\
&= C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\left(\frac{1}{m^*}\right)^3 CB^2, \\
S_3 &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\frac{BC^2}{1\cdot 2\cdot(-1)}.
\end{aligned} \tag{24}$$

For way (IV), we have

$$E_i - E_{m_1} = \hbar\omega, \quad E_i - E_{m_2} = 2\hbar\omega, \quad E_i - E_{m_3} = 3\hbar\omega;$$

$$\begin{aligned}
&\langle i|\hat{H}_{\rm el} + \hat{H}_{\rm ep}|m_1\rangle\langle m_1|\hat{H}_{\rm el} + \hat{H}_{\rm ep}|m_2\rangle\langle m_2|\hat{H}_{\rm el} + \hat{H}_{\rm ep}|f\rangle \\
&= C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\left(\frac{1}{m^*}\right)^3 C^3, \\
S_4 &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\frac{C^3}{1\cdot 2\cdot 3}.
\end{aligned} \tag{25}$$

Substituting Eqs. (22)–(25) in into Eq. (3), we have

$$\begin{aligned}
S &= S_1 + S_2 + S_3 + S_4 + 0 \\
&= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\left(\frac{B^3}{(-3)\cdot(-2)\cdot(-1)} + \frac{B^2C}{1\cdot(-2)\cdot(-1)} + \frac{BC^2}{1\cdot 2\cdot(-1)} + \frac{C^3}{1\cdot 2\cdot 3}\right) \\
&= -\frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\frac{1}{3!}(B^3 - 3BC^2 + 3C^2B - C^3) \\
&= -\frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^3\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}}{(\hbar\omega)^3(m^*)^3}\frac{1}{3!}(B-C)^3.
\end{aligned} \tag{26}$$

Using the same rules as those we have introduced above, we obtain the following diagram for three-photon absorption (to show the calculation law clearly, we make some labels on it).

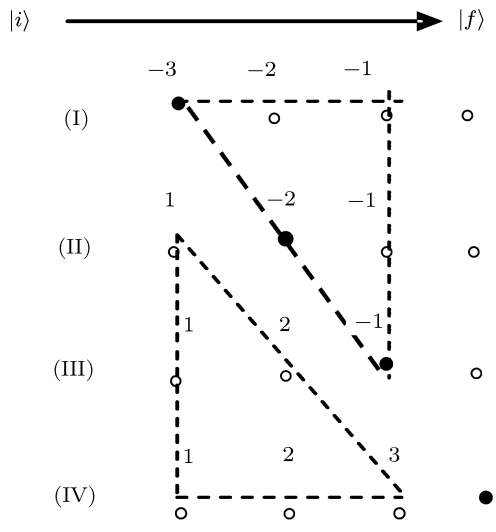


Fig. 3. Diagram for three-photon absorption.

3.4. Phonon-assisted four-photon absorption

For four-photon absorption process, there are five ways from $|i\rangle \to |f\rangle$. Repeating the above calculation process, we obtain the fellowing diagram:

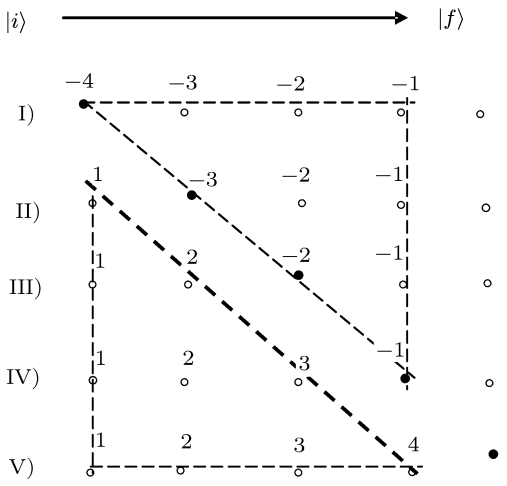


Fig. 4. Diagram for four-photon absorption.

According to the rules introduced above, the transition element for four-photon absorption now can be easily obtained as

$$\begin{aligned} S &= S_1 + S_2 + S_3 + S_4 + S_5 + 0 \\ &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^4\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}}{(\hbar\omega)^4(m^*)^4} \\ &\quad \times \left(\frac{B^4}{(-4)\cdot(-3)\cdot(-2)\cdot(-1)} + \frac{B^3C}{1\cdot(-3)\cdot(-2)\cdot(-1)} + \frac{B^2C^2}{1\cdot2\cdot(-2)\cdot(-1)} + \frac{BC^3}{1\cdot2\cdot3\cdot(-1)} + \frac{C^4}{1\cdot2\cdot3\cdot4}\right) \\ &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^4\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}}{(\hbar\omega m^*)^4}\frac{1}{4!}(B-C)^4, \end{aligned} \tag{27}$$

where the expression

$$\frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^4\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}}{(\hbar\omega)^4(m^*)^4}$$

is the common factor in S_1, S_2, S_3, S_4 and S_5 (in phonon-assisted four-photon absorption process, the annihilation operator of photon $b_{\boldsymbol{k}_l}$ is used four times and the annihilation operator of phonon is used once. Thus, it is easy to obtain the factor

$$\frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^4\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}}{(\hbar\omega m^*)^4}$$

in Eq. (27)).

3.5. Phonon-assisted *n*-photon absorption

For n-photon absorption, there are $n+1$ ways from $|i\rangle \to |f\rangle$ and the diagram for n-photon absorption is as follows:

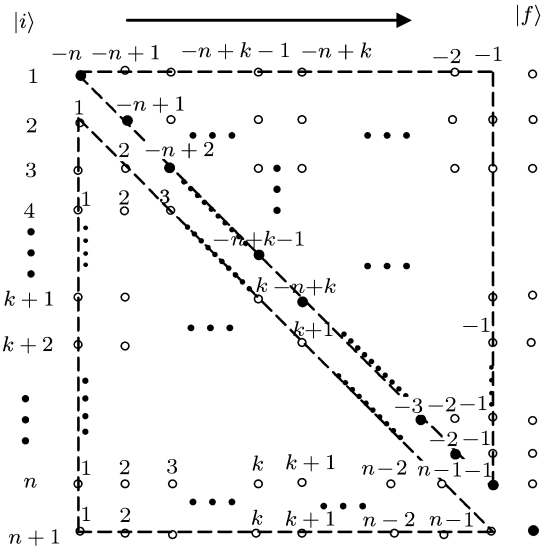


Fig. 5. Diagram for n photon absorption.

The transition element for n-photon absorption is

$$\begin{aligned} S &= S_1 + S_2 + S_3 + \cdots S_k + S_{k+1}\cdots + S_n + S_{n+1} \\ &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^n\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}\cdots\sqrt{m-n+1}}{(\hbar\omega)^n(m^*)^n} \\ &\quad \times \left(\frac{B^n}{(-1)^n n\cdot(n-1)\cdot(n-2)\cdots1} + \frac{CB^{n-1}}{(-1)^{n-1}\cdot1\cdot(n-1)\cdot(n-2)\cdots1} + \frac{C^2B^{n-2}}{(-1)^{n-2}\cdot1\cdot2\cdot(n-2)\cdots1}\right. \\ &\quad + \cdots\frac{C^kB^{n-k}}{(-1)^{n-k}\cdot1\cdot2\cdots k\cdot(n-k)\cdot(n-k+1)\cdots1} \\ &\quad \left. + \frac{C^{k+1}B^{n-k-1}}{(-1)^{n-k-1}\cdot1\cdot2\cdots k\cdot(k+1)\cdot(n-k-1)\cdot(n-k+1)\cdots1} + \cdots\frac{C^n}{1\cdot2\cdot3\cdots n}\right) \\ &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^n\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}\cdots\sqrt{m-n+1}}{(\hbar\omega)^n(m^*)^n}\times\frac{(-1)^n}{n!} \\ &\quad \times (B^n + \frac{n!B^{n-1}(-C)}{(n-1)!1!} + \frac{n!B^{n-2}(-C)^2}{(n-2)!2!} + \cdots + \frac{n!B^{n-k}(-C)^k}{(n-k)!k!} + \cdots(-C)^n) \\ &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^n\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}\cdots\sqrt{m-n+1}}{(\hbar\omega)^n}\times\frac{(-1)^n}{n!}\sum_0^n\frac{n!B^{n-k}(-C)^k}{(n-k)!k!} \\ &= \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^n\sqrt{m}\,\sqrt{m-1}\sqrt{m-2}\sqrt{m-3}\cdots\sqrt{m-n+1}}{(\hbar\omega)^n}\times\frac{(-1)^n}{n!}(B-C)^n, \end{aligned} \tag{28}$$

where the binomial theorem

$$(x+y)^n = \sum_{k=0}^{n} \frac{n! x^{n-k} y^k}{(n-k)!k!}$$

has been used. If we take $m - n \approx m \sim A^2$, equation (28) then becomes

$$\begin{aligned} S &\approx \frac{C_{\rm ep}\sqrt{n_{\rm p}}(C_{\rm el})^n \sqrt{m}\,\sqrt{m}\,\sqrt{m}\,\sqrt{m}\cdots\sqrt{m}}{(\hbar\omega)^n (m^*)^n} \times \frac{(-1)^n}{n!}(B-C)^n \\ &= C_{\rm ep}\sqrt{n_{\rm p}}\left(\frac{e\boldsymbol{A}_0\cdot(\hbar\boldsymbol{k}_f - \hbar\boldsymbol{k}_i)}{2(\hbar\omega)m^*}\right)^n \times \frac{(-1)^n}{n!} = C_{\rm ep}\sqrt{n_{\rm p}}\left(\frac{e\boldsymbol{A}_0\cdot(\boldsymbol{P}_f - \boldsymbol{P}_i)}{\hbar\omega m^*}\right)^n \frac{(-1)^n}{2^n n!}. \end{aligned} \tag{29}$$

Equation (29) is the general transition element of phonon-assisted n-photon absorption. It can be found that the expression $\left(\frac{e\boldsymbol{A}_0\cdot(\boldsymbol{P}_f - \boldsymbol{P}_i)}{\hbar\omega m^*}\right)^n \frac{(-1)^n}{2^n n!}$ in the above equation is just the first term of the n-th order first kind Bessel function $\mathrm{J}_n\left(\frac{e\boldsymbol{A}_0\cdot(\boldsymbol{P}_f - \boldsymbol{P}_i)}{\hbar\omega m^*}\right)$.[17] Finally, we obtain the transition rate for n-photon absorption as (where $n<0$ for the emission of photons)

$$\begin{aligned} W &= \frac{2\pi}{\hbar}\int |S|^2 \delta(E_f - E_i)\mathrm{d}\boldsymbol{S}_f \\ &= \frac{2\pi}{\hbar}\int |C_{\rm ep}\sqrt{n_{\rm p}}|^2 \left|\left(\frac{e\boldsymbol{A}_0\cdot(\boldsymbol{P}_f - \boldsymbol{P}_i)}{\hbar\omega m^*}\right)^n \frac{1}{2^n n!}\right|^2 \delta\left(\frac{P_f^2 - P_i^2}{2m^*} - \hbar\omega_{\rm p} - n\hbar\omega\right)\frac{V}{(2\pi\hbar)^3}\mathrm{d}\boldsymbol{P}_f. \end{aligned} \tag{30}$$

It should be noted that the above equation is for the phonon absorption process. In the case of phonon emission process, the phonon occupation number $n_{\rm p}$ and $-\hbar\omega_{\rm p}$ should be replaced by $n_{\rm p}+1$ and $\hbar\omega_{\rm p}$, respectively.

4. Summary

With the help of a diagram approach which is proposed in this work, we obtained a general formula for phonon-assisted n-photon absorption in solids. The obtained general formula has a simple form that can be conveniently employed to investigate the phonon-assisted multi-photon process in solids.

Appendix A

The time evolution operator of Eq. (1) in the interaction picture (or Dirac picture) can be written in the following form:[18]

$$\begin{aligned} U(t,0) = 1 &+ \left(-\frac{\mathrm{i}}{\hbar}\right)\int_0^t \hat{V}'(t')\mathrm{d}t' + \left(\frac{-\mathrm{i}}{\hbar}\right)^2 \int_0^t \hat{V}'(t')\mathrm{d}t' \int_0^{t'} \hat{V}'(t'')\mathrm{d}t'' \\ &+ \left(-\frac{\mathrm{i}}{\hbar}\right)^3 \int_0^t \hat{V}'(t')\mathrm{d}t' \int_0^{t'} \hat{V}'(t'')\mathrm{d}t'' \int_0^{t''} \hat{V}'(t''')\mathrm{d}t''' + \cdots \\ &= 1 + U^{(1)} + U^{(2)} + U^{(3)} \cdots, \end{aligned} \tag{A1}$$

where,

$$\hat{V}'(t) = \exp\left(\frac{\mathrm{i}}{\hbar}\hat{H}_0 t\right)\hat{V}(t)\exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t\right).$$

If the initial state ($t=0$) is in eigenstate $|i\rangle$ of Hamiltonian $\hat{H}_0$ and the final state is in another eigenstate $|f\rangle$ of $\hat{H}_0$, the transition rate from initial sate $|i\rangle$ to the final state $|f\rangle$ can be calculated with the following procedures.

A1. First order perturbation

For the first order perturbation, the transition amplitude is in the following form:

$$C_{fi} = \langle f|U^{(1)}|i\rangle = -\frac{\mathrm{i}}{\hbar}\int_0^t \langle f|\exp\left(\frac{\mathrm{i}}{\hbar}\hat{H}_0 t\right)\hat{V}\exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t\right)|i\rangle \mathrm{d}t'$$

$$= -V_{fi}\frac{1}{E_f - E_i}\left\{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_i)t\right] - 1\right\}, \tag{A2}$$

where $V_{fi} = \langle f|\hat{V}|i\rangle$. And the transition rate for $|i\rangle \to |f\rangle$ can be expressed as

$$W = \lim_{t\to\infty}\frac{|\langle f|U^{(1)}|i\rangle|^2}{t} = |V_{fi}|^2 \lim_{t\to\infty}\frac{2\left[1 - \cos\frac{1}{\hbar}(E_f - E_i)t\right]}{t(E_f - E_i)^2}. \tag{A3}$$

Because

$$\lim_{t\to\infty}\frac{\left[1 - \cos\frac{1}{\hbar}(E_f - E_i)t\right]}{\pi t\left(\frac{E_f - E_i}{\hbar}\right)^2} = \frac{2}{\pi}\lim_{t\to\infty}\frac{\sin^2(xt/2)}{tx^2} = \delta(x), \tag{A4}$$

where $x = (E_f - E_i)/\hbar$, we have

$$W = \frac{2\pi}{\hbar^2}|V_{fi}|^2\delta\left(\frac{E_f - E_i}{\hbar}\right). \tag{A5}$$

A2. Second order perturbation

If $\langle f|U^{(1)}|i\rangle = 0$, we need to consider the second order perturbation. The second term in Eq. (A1) is

$$\begin{aligned} U^{(2)} &= \left(\frac{-\mathrm{i}}{\hbar}\right)^2\int_0^t \hat{V}'(t')\mathrm{d}t'\int_0^{t'}\hat{V}'(t'')\mathrm{d}t'' \\ &= \left(-\frac{\mathrm{i}}{\hbar}\right)^2\int_0^t \exp\left(\frac{\mathrm{i}}{\hbar}\hat{H}_0 t'\right)\hat{V}(t')\exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t'\right)\mathrm{d}t'\int_0^{t'}\exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t''\right)\hat{V}(t'')\exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t''\right)\mathrm{d}t''. \end{aligned} \tag{A6}$$

To calculate $\langle f|U^{(2)}|i\rangle$, a completeness relation

$$\sum_n |n\rangle\langle n| = 1 \tag{A7}$$

needs to be added into the calculation process, where $|n\rangle$ is the eigenstate of $\hat{H}_0$ and it is called intermediate state (not a real state). The transition amplitude for the second order perturbation can be written as

$$\begin{aligned} C_{fi} = \langle f|U^{(2)}|i\rangle &= \left(\frac{-i}{\hbar}\right)^2\langle f|\int_0^t \hat{V}'(t')\mathrm{d}t'\int_0^{t'}\sum_n |n\rangle\langle n|\hat{V}'(t'')\mathrm{d}t''|i\rangle \\ &= \left(-\frac{\mathrm{i}}{\hbar}\right)^2\sum_n V_{fn}V_{ni}\int_0^t \mathrm{d}t'\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_n)t'\right]\int_0^{t'}\mathrm{d}t''\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_n)t''\right] \\ &= \left(\sum_n V_{fn}V_{ni}\frac{1}{E_n - E_i}\right)\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_i)t\right] - 1}{E_f - E_i} - \sum_n\left(\frac{V_{fn}V_{ni}}{E_n - E_i}\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_n)t\right] - 1}{E_f - E_n}\right) \\ &= A_1 + B_1, \end{aligned} \tag{A8}$$

where

$$A_1 = \left(\sum_n V_{fn}V_{ni}\frac{1}{E_n - E_i}\right)\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_i)t\right] - 1}{E_f - E_i}, \quad \text{and} \quad B_1 = -\sum_n\left(\frac{V_{fn}V_{ni}}{E_n - E_i}\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f - E_n)t\right] - 1}{E_f - E_n}\right).$$

For the second order perturbation, the transition rate is

$$W = \lim_{t\to\infty}\frac{|A_1 + B_1|^2}{t} = \lim_{t\to\infty}\frac{|A_1|^2}{t} + \lim_{t\to\infty}\frac{A_1^*B_1 + A_1B_1^* + |B_1|^2}{t}. \tag{A9}$$

Because

$$\lim_{t\to\infty}\frac{\left(\exp\left[\pm\frac{\mathrm{i}}{\hbar}(E_f-E_i)t\right]-1\right)}{t(E_f-E_i)}\frac{\left(\exp\left[\mp\frac{\mathrm{i}}{\hbar}(E_f-E_n)\right]-1\right)}{E_f-E_n}=0, \tag{A10}$$

$$\lim_{t\to\infty}\frac{1}{t}\left|\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f-E_n)\right]-1}{E_f-E_n}\right|^2=0, \tag{A11}$$

we have

$$W=\lim_{t\to\infty}\frac{|A_1+B_1|^2}{t}=\lim_{t\to\infty}\frac{|A_1|^2}{t}+0=\frac{2\pi}{\hbar^2}\left|\sum_n\frac{V_{ni}V_{fn}}{E_i-E_n}\right|^2\delta\left(\frac{E_f-E_i}{\hbar}\right), \tag{A12}$$

where E_n is the corresponding eigenvalue of the intermediate state $|n\rangle$.

A3. Third order perturbation

If $\langle f|U^{(2)}|i\rangle=0$, we need to consider the third order perturbation

$$U^{(3)}=\left(-\frac{\mathrm{i}}{\hbar}\right)^3\int_0^t\hat{V}'(t')\mathrm{d}t'\int_0^{t'}\hat{V}'(t'')\mathrm{d}t''\int_0^{t''}\hat{V}'(t''')\mathrm{d}t'''. \tag{A13}$$

To calculate $\langle f|U^{(3)}|i\rangle$, two completeness relations

$$\sum_n|n\rangle\langle n|=1\quad\text{and}\quad\sum_m|m\rangle\langle m|=1 \tag{A14}$$

are added into the calculation process, where $|m\rangle$ is another intermediate state. The transition amplitude for the third order perturbation is

$$\begin{aligned}C_{fi}=\langle f|U^{(3)}|i\rangle&=\left(-\frac{\mathrm{i}}{\hbar}\right)^3\langle f|\int_0^t\hat{V}'(t')\mathrm{d}t'\int_0^{t'}\sum_m|m\rangle\langle m|\hat{V}'(t'')\mathrm{d}t''\int_0^{t''}\sum_n|n\rangle\langle n|\hat{V}'(t''')\mathrm{d}t'''|i\rangle\\&=-\left(\sum_{n,m}\frac{V_{fm}V_{mn}V_{ni}}{(E_m-E_i)(E_n-E_i)}\right)\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f-E_i)t\right]-1}{E_f-E_i}+B_2=A_2+B_2,\end{aligned} \tag{A15}$$

where B_2 is another part of $\langle f|U^{(3)}|i\rangle$. For the third order perturbation, the transition rate is

$$W=\lim_{t\to\infty}\frac{\langle f|U^{(3)}|i\rangle}{t}=\lim_{t\to\infty}\frac{|A_2+B_2|^2}{t}=\lim_{t\to\infty}\frac{|A_2|^2}{t}+\lim_{t\to\infty}\frac{A_2^*B_2+A_2B_2^*+|B_2|^2}{t}. \tag{A16}$$

Similar to the second order perturbation, only the term which contains the factor $\lim_{t\to\infty}\left|\frac{\exp\left[\frac{\mathrm{i}}{\hbar}(E_f-E_i)t\right]-1}{E_f-E_i}\right|$ has the contribution to Eq. (A16). So equation (A16) now can be written as

$$W=\lim_{t\to\infty}\frac{\langle f|U^{(3)}|i\rangle}{t}=\lim_{t\to\infty}\frac{|A_2|^2}{t}=\frac{2\pi}{\hbar^2}\left|\sum_{n,m}\frac{V_{fm}V_{mn}V_{ni}}{(E_i-E_m)(E_i-E_n)}\right|^2\delta\left(\frac{E_f-E_i}{\hbar}\right). \tag{A17}$$

It can be found that the third order perturbation transition element is

$$S=\sum_{n,m}\frac{V_{fm}V_{mn}V_{ni}}{(E_i-E_m)(E_i-E_n)}=\sum_{n,m}\frac{\langle f|V|m\rangle\langle m|V|n\rangle\langle n|V|i\rangle}{(E_i-E_m)(E_i-E_n)}. \tag{A18}$$

A4. $(n+1)$-th order perturbation

Repeating the above calculation process, the transition rate expression for the $(n+1)$-th order perturbation can be summarized as

$$W = \frac{2\pi}{\hbar^2}\left|\sum_{m_1,m_2,\ldots,m_n} \frac{\langle f|\hat{V}|m_n\rangle\cdots\langle m_K|\hat{V}|m_{K-1}\rangle\cdots\langle m_2|\hat{V}|m_1\rangle\langle m_1|\hat{V}|i\rangle}{(E_i-E_{m_1})\cdots(E_i-E_K)\cdots(E_i-E_{m_n})}\right|^2 \delta\left(\frac{E_f-E_i}{\hbar}\right), \tag{A19}$$

where $|m_1\rangle$, $|m_2\rangle$,..., $|m_n\rangle$ denote the intermediate states, and E_{m_1}, $E_{m_2},\ldots,E_{m_n}$ refer to the corresponding intermediate energies. In Eq. (A19), the transition element is in the following form:

$$S = \sum_{m_1,m_2,\ldots,m_n} \frac{\langle f|\hat{V}|m_n\rangle\cdots\langle m_K|\hat{V}|m_{K-1}\rangle\cdots\langle m_2|\hat{V}|m_1\rangle\langle m_1|\hat{V}|i\rangle}{(E_i-E_{m_1})\cdots(E_i-E_K)\cdots(E_i-E_{m_n})}. \tag{A20}$$

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