

## Chapter 5

# Theory to Nonresonant Multiphoton Transitions (NMT)

Nonresonant multiphoton transitions (NMT) [73] are a common phenomenon that occur in many types of molecules. The theory of femtosecond spectroscopy can benefit from the inclusion of NMT because these transitions play a significant role in population transfer. These types of transitions take place if the energy of two or more photons is necessary to achieve an electronic excitation, where no intermediate states exist which facilitate single-photon transitions. The absence of intermediate states indicates that coupling matrix elements to the multitude of high-lying, off-resonant states are very important. Although NMT processes have been extensively considered in the frequency domain, attempts in the femtosecond time regime have been limited [34, 35, 36, 37].

As shown in the last chapter, several laser pulse control experiments on polyatomic systems have been recently demonstrated [19, 27, 115, 116, 117, 118, 119]. In particular ref. [27] shows that NMT can be a route to achieve control of molecular dynamics. Taking both NMT and control experiments into account, the aim of this chapter is to develop a theory for the description of NMT which can be combined to optimal control theory (OCT) [120, 121]. The structure of this chapter starts with the model which will be applied to two descriptions of NMT: a perturbative and a nonperturbative approach. The perturbative approach, which is limited to the low-field regime and therefore not applicable to standard OCT, will give some insight into the development of the nonperturbative approach, which, by solving the exact form of the TDSE, accounts for the strong-field

regime and is incorporated into OCT.

The theory of NMT [120] has been developed by PD Dr. May at the Humboldt University Berlin and has been applied in this work.

## 5.1 The Model

This section introduces the model for the description of NMT. In this work, the nonadiabatic couplings have been neglected, since they are not relevant for the chosen electronic states of the molecular system. For the sake of completeness, the TDSE is given below

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{\mathbf{H}}(t)|\Psi(t)\rangle, \quad (5.1)$$

where the complete Hamiltonian

$$\hat{\mathbf{H}}(t) = \hat{\mathbf{H}}_{\text{mol}} + \hat{\mathbf{H}}_{\text{field}}(t), \quad (5.2)$$

is composed of the molecular  $\hat{\mathbf{H}}_{\text{mol}}$  and the field  $\hat{\mathbf{H}}_{\text{field}}(t)$  Hamiltonians, which was previously denoted as  $\hat{\mathbf{V}}(t)$  (see eq. 3.15). The expansion of the molecular Hamiltonian with respect to the adiabatic electronic states,  $|\varphi_a\rangle$ , formerly defined as  $|\Psi_{\text{el}}(\mathbf{r}_a; \mathbf{R}_A)\rangle$  from eq. 2.4, is given as

$$\hat{\mathbf{H}}_{\text{mol}} = \sum_a \hat{H}_a(q)|\varphi_a\rangle\langle\varphi_a|, \quad (5.3)$$

where  $\hat{H}_a(q)$  are the respective vibrational Hamiltonians and  $q$  is the set of vibrational coordinates. The eigenvalues  $\epsilon_{aM}$  are given as

$$\epsilon_{aM} = \epsilon_a + \omega_{aM} \quad \text{where} \quad M = 0, 1, 2, \dots, \quad (5.4)$$

where the electronic quantum numbers are denoted by the index  $a$  and the vibrational quantum numbers by the index  $M$ . The electronic reference energy, i.e. the minimum value of the PES plus the zero point energy is given as  $\epsilon_{aM}$ . The vibrational eigenfunctions are depicted as  $|\chi_{aM}\rangle$ , previously denoted as  $|\Psi_{\text{el},j}^v\rangle$ , see section 2.3.1.

The second part of eq. 5.2, which describes the coupling to the radiation field, is given by the standard dipole approximation as

$$\hat{\mathbf{H}}_{\text{field}}(t) = -\mathbf{E}(t)\hat{\boldsymbol{\mu}} \equiv -\mathbf{E}(t) \sum_{a,b} \boldsymbol{\mu}_{ab}|\varphi_a\rangle\langle\varphi_b| + \text{h.c.}, \quad (5.5)$$

where  $\hat{\boldsymbol{\mu}}$  is the molecular dipole operator, and  $\boldsymbol{\mu}_{ab}$  are the electronic dipole matrix elements, see eq. 3.35, and  $\mathbf{E}(t)$  is the electric field which is written here as

$$\mathbf{E}(t) = \frac{1}{2} \mathbf{n} E(t) e^{-i\omega t} + \text{c.c.}, \quad (5.6)$$

where  $\mathbf{n}$  is the linear polarization unit vector,  $E(t)$  is the field envelope, and  $\omega$  is the carrier frequency. The field envelope

$$E(t) = E_0 \sin^2 \left( \frac{t\pi}{t_p} \right) \quad \text{for} \quad t_0 \leq t \leq t_p \quad (5.7)$$

defines the field shape as a sine squared function, the field amplitude is denoted as  $E_0$ , and the pulse duration,  $t_p$ . The abbreviations h.c. and c.c. found in eqs. 5.5 and 5.6 are the hermitian conjugate and the complex conjugate respectively. The formal solution to eq. 5.1, which evolves the initial wave function  $\Psi(t_0)$  in time, is given as

$$|\Psi(t)\rangle = U_{\text{mol}}(t - t_0) S(t, t_0; \mathbf{E}) |\Psi(t_0)\rangle, \quad (5.8)$$

where  $U_{\text{mol}}(t - t_0)$  is the field-free evolution operator

$$U_{\text{mol}}(t - t_0) = \exp \left( - \frac{i}{\hbar} \hat{\mathbf{H}}_{\text{mol}}(t - t_0) \right) \quad (5.9)$$

and the  $S$ -operator,  $S(t, t_0; \mathbf{E})$ , couples the radiation field to the molecular system

$$S(t, t_0; \mathbf{E}) = \hat{T} \exp \left( - \frac{i}{\hbar} \int_{t_0}^t d\tau \underbrace{U_{\text{mol}}^\dagger(\tau - t_0) \hat{\mathbf{H}}_{\text{field}}(\tau) U_{\text{mol}}(\tau - t_0)}_{-\hat{\boldsymbol{\mu}}(\tau) \mathbf{E}(\tau)} \right), \quad (5.10)$$

where  $\hat{T}$  is the time ordering operator [74]. The field Hamiltonian is defined in the interaction picture, and therefore the transition dipole moment becomes time dependent. The  $S$ -operator can be expanded as

$$S(t, t_0; \mathbf{E}) = 1 + S^{(1)}(t, t_0; \mathbf{E}) + S^{(2)}(t, t_0; \mathbf{E}) + \dots \quad (5.11)$$

The first order expansion of the  $S$ -matrix is defined as

$$S^{(1)}(t, t_0; \mathbf{E}) = \frac{i}{\hbar} \int_{t_0}^t d\tau \hat{\boldsymbol{\mu}}(\tau) \mathbf{E}(\tau), \quad (5.12)$$

and the second order expansion is given as

$$S^{(2)}(t, t_0; \mathbf{E}) = - \frac{1}{\hbar^2} \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \hat{\boldsymbol{\mu}}(\tau_1) \mathbf{E}(\tau_1) \hat{\boldsymbol{\mu}}(\tau_2) \mathbf{E}(\tau_2). \quad (5.13)$$

## 5.2 Perturbative Approach

Nonresonant multiphoton processes have been described in the perturbative framework [39, 122]. The perturbation order is determined by the power of the field strength upon a Taylor expansion of the S-operator. Each power of the field strength corresponds to the number of photons involved in the transition.

Multiphoton transitions can be described in terms of the expansion coefficients which are obtained in the following. The state function is expanded in terms of all the electronic and vibrational basis and gives

$$|\Psi(t)\rangle = \sum_{a,M} C_{aM}(t) |\Psi_{aM}\rangle, \quad (5.14)$$

where the wave function,

$$|\Psi_{aM}\rangle = |\chi_{aM}\rangle |\varphi_a\rangle \quad (5.15)$$

is composed of the vibrational  $|\chi_{aM}\rangle$  and electronic  $|\varphi_a\rangle$  wave functions, and  $C_{aM}(t)$  are the time-dependent expansion coefficients. The indices denote the set of electronic quantum numbers ( $a = g, f, \dots$ ) and the vibrational quantum numbers ( $M = 0, 1, 2, \dots$ ). Multiplying eq. 5.14 by the electronic-vibrational state  $\langle\Psi_{fN}|$  from the left and rearranging the expression in terms of the expansion coefficients, in which the initial state is taken as the ground vibrational state in the ground electronic state  $|\Psi_{g0}\rangle$ , results in

$$C_{fN}(t) = e^{-i\omega_{fN}(t-t_0)} \langle\Psi_{fN}|S(t, t_0; \mathbf{E})|\Psi_{g0}\rangle. \quad (5.16)$$

Moreover, the time-dependent expansion coefficients contain information on the vibrational wavepacket dynamics induced by this transition. Single photon transitions are described by eq. 5.16 by replacing the S-operator by its first order term, see eq. 5.12. In the same manner, two photon nonresonant transitions can be described within perturbation theory [34] in which the complete S-operator in eq. 5.16 is replaced by the second order contribution of the S-operator expansion eq. 5.13. The matrix elements for the coefficient expression in eq. 5.16 are given as

$$\langle\Psi_{fN}|S^{(2)}(t, t_0; \mathbf{E})|\Psi_{gM}\rangle = -\frac{1}{\hbar^2} \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \langle\Psi_{fN}|[\mathbf{E}(\tau_1)\hat{\boldsymbol{\mu}}(\tau_1)][\mathbf{E}(\tau_2)\hat{\boldsymbol{\mu}}(\tau_2)]|\Psi_{gM}\rangle, \quad (5.17)$$

where the ground vibrational state is replaced by the general vibrational quantum number  $M$ . The expansion coefficients for the case of cw-excitation in the frequency domain are obtained in the limit as  $t_0 \rightarrow -\infty$  and are given below for the excited electronic state

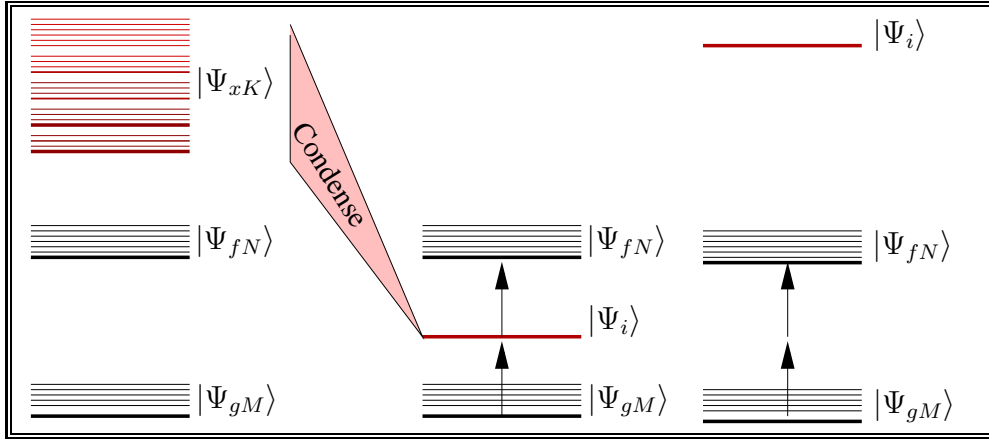
$$C_{fN}(t) = -e^{-i\omega_{fN}(t-t_0)-i2\omega t_0} \frac{E^2}{4\hbar^2} \sum_{xK} \frac{\mu(fN, xK)\mu(xK, gM)}{\omega_{xK} - \omega_{gM} - \omega} \times \left( \frac{1}{\omega_{fN} - \omega_{gM} - 2\omega + i\epsilon} - \frac{1}{\omega_{fN} - \omega_{xK} - \omega + i\epsilon} \right), \quad (5.18)$$

where the electric field  $\mathbf{E}(t)$ , eq. 5.6, is replaced with the contribution,  $e^{-i\omega t}$ , and  $E$  is the constant field envelope. The sum over  $xK$  accounts for all of the off-resonant electronic-vibrational states. The dipole transition matrix elements are given in general as,  $\mu(aN, bM) = \langle \Psi_{aN} | \mathbf{n}\hat{\boldsymbol{\mu}} | \Psi_{bM} \rangle$ , and include the unit vector  $\mathbf{n}$ .

The terms of the expansion coefficients from eq. 5.18 can be best understood by applying the sketch in fig. 5.1. The left set of electronic states is used to describe a complete description of a molecular system. If the off-resonant terms are condensed into a single electronic state  $|\Psi_i\rangle$  which is placed conveniently between the initial ground electronic state  $|\Psi_{gM}\rangle$  and the excited electronic state  $|\Psi_{fN}\rangle$ , as depicted in the second set of states in fig. 5.1, then the second term in eq. 5.18 describes the step-wise population transfer from the ground state to the intermediate state,  $|\Psi_{gM}\rangle \rightarrow |\Psi_i\rangle$  and then from the intermediate state to the final excited state,  $|\Psi_i\rangle \rightarrow |\Psi_{fN}\rangle$ , both transitions occurring via a single-photon absorption process. The first term in eq. 5.18 is responsible for a direct transition from the ground state,  $|\Psi_{gM}\rangle$ , to the excited state,  $|\Psi_{fN}\rangle$ , without support of intermediate states,  $|\Psi_i\rangle$ , and gives a resonant contribution regardless of the position of  $|\Psi_i\rangle$ , as can be seen in the representation on the far-right in fig. 5.1. In this representation, because  $|\Psi_i\rangle$  is placed energetically far above  $|\Psi_{fN}\rangle$ , the first term in eq. 5.18 decreases in  $1/\omega_i$  ( $\equiv 1/\omega_{xK}$ ) and the second in  $1/\omega_i^2$  ( $\equiv 1/\omega_{xK}^2$ ), where  $\omega_{xK}$  is the transition frequency into the off-resonant electronic states. Hence, it is the first term that strongly dominates and therefore the second term will be neglected in the following.

If the single state  $|\Psi_i\rangle$  is replaced now by the manifold of electronic-vibrational states belonging to the off-resonant electronic states  $|\Psi_{xK}\rangle$ , then the smallness of the overall sum of the expansion coefficients in eq. 5.18 can be compensated for by introducing the density of states for the manifold of states

$$\varrho(\Omega) = \sum_{x,K} \delta(\Omega - \omega_{xK}), \quad (5.19)$$



**Figure 5.1:** A schematic representation of the ground  $|\Psi_{gM}\rangle$  and excited  $|\Psi_{fN}\rangle$  electronic states, with the manifold of off-resonant states  $|\Psi_{xK}\rangle$ , used to describe eq. 5.18. The first subfigure depicts the complete space for a molecular system. The second set of states depict a two-photon transition from the ground state  $|\Psi_{gM}\rangle$  to the excited state  $|\Psi_{fN}\rangle$ . The off-resonant states  $|\Psi_{xK}\rangle$  have been condensed into a single intermediate state  $|\Psi_i\rangle$ , and placed directly between the two states to support the transition. The last set of electronic states depicts a direct nonresonant two-photon transition without the aid of the intermediate state  $|\Psi_i\rangle$ , which has been moved to higher energetic values.

where the eigenvalue  $\omega_{xK}$  of the off-resonant states is typically not known, and  $|\Psi_{xK}\rangle$  the electronic-vibrational states are spread into a density of final states. Implementing the density of states into the expression for the expansion coefficients, eq. 5.18, yields

$$C_{fN}(t) = -\frac{e^{-i\omega_{fN}(t-t_0)-i2\omega t_0}}{\omega_{fN} - \omega_{gM} - 2\omega + i\epsilon} \frac{E^2}{\hbar^2} \int d\Omega \varrho(\Omega) \frac{\mu(fN, \Omega)\mu(\Omega, gM)}{\Omega - \omega_{gM} - \omega}, \quad (5.20)$$

where  $\mu(fN, \Omega)$  and  $\mu(\Omega, gM)$  denote frequency-dependent, transition dipole operator matrix elements. The expression indicates that the efficiency of the nonresonant two-photon transition, i.e. the population  $|C_{fN}(t)|^2$  of the excited electronic-vibrational state, is essentially determined by the  $\Omega$ -integral. It represents a summation of all off-resonant single-photon transitions from the initial state with energy  $\hbar\omega_{gM}$  into the nonresonant states with energy  $\hbar\Omega$ , and can be viewed as an effective two-photon transition matrix element coupled to the square of the field strength. Consequently, only the complete summation of all these nonresonant contributions may lead to a sufficiently large two-photon transition amplitude.

## 5.3 Nonperturbative Approach

Because any power of the field strength is allowed when considering multiphoton transitions, it is necessary to move to a description that includes the strong-field regime. This regime can be accounted for by solving the TDSE completely. This method has been demonstrated for diatomic molecules at fixed-nuclear distances [123, 124] as well as for one-dimensional model systems where the Born-Oppenheimer Approximation was avoided [125, 126, 127]. Solving the TDSE with inclusion of the ground and all excited electronic states for a molecular system would provide information on every optical transition, including nonresonant multiphoton transitions: nonresonant population transfer, multiphoton ionization, and high harmonic generation. However, this is not possible for polyatomic molecules, due to computational restrictions, and therefore in order to apply the essence of this method to nonresonant multiphoton transitions an effective Hamiltonian is derived.

### 5.3.1 Effective Schrödinger Equation for NMT Processes

The restriction to the number of excited states that can be calculated for polyatomic molecules, prevents a description in which its TDSE can be solved exactly, for NMT processes. Therefore, the complete space is divided into a portion which describes the attainable states; the primary state space (denoted by the index  $a$ ), and a portion which describes the other states; the secondary state space (denoted by the index  $x$ ). This division of the complete space is accomplished by introducing a projection operator, or projector for short, for each space [74],

$$\hat{P} = \sum_a |\varphi_a\rangle\langle\varphi_a| \quad (5.21)$$

$$\hat{Q} = \sum_x |\varphi_x\rangle\langle\varphi_x| \quad (5.22)$$

where the operators  $\hat{P}$  and  $\hat{Q}$  are defined as a complete sum of states in their respective primary and secondary space. The projection operators together form a complete space and  $\hat{P} + \hat{Q} = 1$ . By applying the projectors onto an arbitrary state in the Hilbert space one obtains the primary  $|\Psi_1\rangle$  and secondary  $|\Psi_2\rangle$  states.

$$|\Psi(t)\rangle = (\hat{P} + \hat{Q})|\Psi(t)\rangle = \hat{P}|\Psi(t)\rangle + \hat{Q}|\Psi(t)\rangle = |\Psi_1(t)\rangle + |\Psi_2(t)\rangle \quad (5.23)$$

In the same manner, the reduced Hamiltonians are introduced

$$\hat{P}\hat{\mathbf{H}}(t)\hat{P} = \hat{\mathbf{H}}_1(t) = \hat{\mathbf{H}}_{\text{mol}}^{(1)} + \hat{\mathbf{H}}_{\text{field}}^{(1)}(t) \quad (5.24)$$

$$\hat{Q}\hat{\mathbf{H}}(t)\hat{Q} = \hat{\mathbf{H}}_2(t) = \hat{\mathbf{H}}_{\text{mol}}^{(2)} + \hat{\mathbf{H}}_{\text{field}}^{(2)}(t), \quad (5.25)$$

where  $\hat{\mathbf{H}}_1(t)$  and  $\hat{\mathbf{H}}_2(t)$  are described exclusively in the primary and secondary state space, respectively. In order to obtain an equation that describes the motion of the primary states, the square of the completeness relation is inserted into the TDSE,

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\hat{\mathbf{H}}_{\text{mol}} + \hat{\mathbf{H}}_{\text{field}}(t)\right) \left(\hat{P} + \hat{Q}\right)^2 |\Psi(t)\rangle \quad (5.26)$$

where the  $\hat{P}\hat{Q} = 0$  terms are zero. Multiplying equation 5.26 from the left, once with the primary state projector  $\hat{P}$  and once with the secondary state projector  $\hat{Q}$ , the respective coupled equations are obtained:

$$i\hbar\frac{\partial}{\partial t}|\Psi_1(t)\rangle = \hat{\mathbf{H}}_1(t)|\Psi_1(t)\rangle + \hat{P}\hat{\mathbf{H}}_{\text{field}}(t)\hat{Q}|\Psi_2(t)\rangle \quad (5.27)$$

$$i\hbar\frac{\partial}{\partial t}|\Psi_2(t)\rangle = \hat{\mathbf{H}}_2(t)|\Psi_2(t)\rangle + \hat{Q}\hat{\mathbf{H}}_{\text{field}}(t)\hat{P}|\Psi_1(t)\rangle. \quad (5.28)$$

The mixed terms  $\hat{P}\hat{\mathbf{H}}_{\text{mol}}\hat{Q} = \hat{Q}\hat{\mathbf{H}}_{\text{mol}}\hat{P} = 0$  are also equal to zero. It is assumed that the system is initially located in the ground vibrational of the ground electronic state  $|\Psi_1(t_0)\rangle = |\Psi_{g_0}^{(1)}\rangle$  which belongs to the primary space, and consequently, the initial wave function in the secondary state space is zero,  $|\Psi_2(t_0)\rangle = 0$ . Solving eq. 5.28, under the aforementioned conditions, leads to the solution of the wave function in the secondary state space

$$|\Psi_2(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^t d\bar{t} U_2(t, \bar{t}; \mathbf{E}) \hat{Q}\hat{\mathbf{H}}_{\text{field}}(\bar{t})\hat{P}|\Psi_1(\bar{t})\rangle, \quad (5.29)$$

where the time nonlocality is depicted by  $\bar{t}$ , and is due to the use of the projection operators, and contains a memory effect [128]. The newly appearing time evolution operator is analogous to that given in eq. 5.8, and is given below in terms of time nonlocality:

$$U_2(t, \bar{t}) = U_{\text{mol}}^{(2)}(\bar{t} - t_0) S_2(\bar{t}, t_0; \mathbf{E}). \quad (5.30)$$

The molecular time evolution operator is analogous to eq. 5.9 and is given as

$$U_{\text{mol}}^{(2)}(\bar{t} - t_0) = \exp\left(-\frac{i}{\hbar}\hat{\mathbf{H}}_{\text{mol}}^{(2)}(\bar{t} - t_0)\right). \quad (5.31)$$



The S-operator, which accounts for the field evolution of the wave function, is given below

$$S_2(\bar{t}, t_0; \mathbf{E}) = \hat{T} \exp \left( -\frac{i}{\hbar} \int_{t_0}^{\bar{t}} d\bar{t} U_{\text{mol}}^{\dagger(2)}(\bar{t} - t_0) \hat{\mathbf{H}}_{\text{field}}^{(2)}(\bar{t}) U_{\text{mol}}^{(2)}(\bar{t} - t_0) \right), \quad (5.32)$$

and is similar to eq. 5.10, where  $\hat{\mathbf{H}}_{\text{field}}$  has been replaced with the field Hamiltonian  $\hat{\mathbf{H}}_{\text{field}}^{(2)}$  for the secondary states. Inserting eq. 5.29 into eq. 5.27 results in a closed equation for the primary states  $|\Psi_1\rangle$

$$i\hbar \frac{\partial}{\partial t} |\Psi_1(t)\rangle = \hat{\mathbf{H}}_1(t) |\Psi_1(t)\rangle + \int_{t_0}^t d\bar{t} K_{\text{field}}(t, \bar{t}) |\Psi_1(\bar{t})\rangle. \quad (5.33)$$

where the kernel,  $K_{\text{field}}$ , is defined as

$$K_{\text{field}}(t, \bar{t}) = -\frac{i}{\hbar} \hat{P} \hat{\mathbf{H}}_{\text{field}}(t) \hat{Q} U_{\text{mol}}^{(2)}(t - \bar{t}) S_2(t, \bar{t}; \mathbf{E}) \hat{Q} \hat{\mathbf{H}}_{\text{field}}(\bar{t}) \hat{P} \quad (5.34)$$

and accounts for all NMT processes realized by the coupling to the manifold of secondary states.

### 5.3.2 Weak Field Nonresonant Multiphoton Transition

The solution of  $|\Psi_1(t)\rangle$  is exact and should be identical with  $|\Psi(t)\rangle$  projected onto the primary state space since eq. 5.33 has been derived without applying an approximation. However, in order to solve for the primary states in a concrete example, the kernel must be approximated since the  $K_{\text{field}}$  in eq. 5.34, already includes a complete summation with respect to  $\mathbf{E}$  via  $S_2$ , cf. eqs. 3.26 and 5.32. The kernel is therefore represented as a sum of terms with respect to the order of the field strength and is separated accordingly,

$$K_{\text{field}}(t, \bar{t}) = K_{\text{field}}^{(2)}(t, \bar{t}) + K_{\text{field}}^{(3)}(t, \bar{t}) + \dots, \quad (5.35)$$

where  $K_{\text{field}}^{(2)}$  and  $K_{\text{field}}^{(3)}$  are the respective second and third power terms in the field strength. In order to get an expression that is second order in the field strength,  $S_2$  in eq. 5.34 is set to one;  $S_2(t, \bar{t}; \mathbf{E}) \approx 1$ , and the following is obtained,

$$K_{\text{field}}^{(2)}(t, \bar{t}) = -\frac{i}{\hbar} \hat{P} \hat{\mathbf{H}}_{\text{field}}(t) \hat{Q} U_2^{(\text{mol})}(t - \bar{t}) \hat{Q} \hat{\mathbf{H}}_{\text{field}}(\bar{t}) \hat{P} \quad (5.36)$$

which, due to its second order character of the field Hamiltonian, suggests a description for two-photon transitions. Unfortunately, there is not any specific criterion about which

powers of the field strength  $\mathbf{E}(t)$ , found in the kernel  $K_{\text{field}}^{(2)}$ , are proper for the calculation of the state vector  $\Psi_1(t)$ . In the strong-field regime, there is no way to prove that the dynamics that ensue convey the proper information. In fact, the only criterion that may be applied, as suggested by the limit of perturbation theory, is that the powers of the field strength may only induce a maximum fourth order dependence on the population of the excited state, i.e.  $P_f \sim \mathbf{E}^4$ .

In order to obtain the kernel for the third power of the field strength, a linear expansion of  $S_2(t, \bar{t}; \mathbf{E})$  is taken, which depends on the field Hamiltonian for the secondary states, see eqs. 5.32 and 5.25, and results in

$$K_{\text{field}}^{(3)}(t, \bar{t}) = -\frac{1}{\hbar^2} \int_{\bar{t}}^t dt_1 \hat{P} \hat{\mathbf{H}}_{\text{field}}(t) \hat{Q} U_{\text{mol}}^{(2)}(t - t_1) \hat{Q} \hat{\mathbf{H}}_{\text{field}}(t_1) \hat{Q} U_{\text{mol}}^{(2)}(t_1 - \bar{t}) \hat{Q} \hat{\mathbf{H}}_{\text{field}}(\bar{t}) \hat{P}. \quad (5.37)$$

The electronic matrix elements of the kernel are given below, in a style consistent with the standard form of the electric-dipole terms, written as

$$K_{ab}^{(2)}(t, \bar{t}) = -\boldsymbol{\mu}_{ab}^{(2)}(t - \bar{t}) \mathbf{E}(t) \mathbf{E}(\bar{t}), \quad (5.38)$$

and

$$K_{ab}^{(3)}(t, \bar{t}) = -\int_{\bar{t}}^t dt_1 \boldsymbol{\mu}_{ab}^{(3)}(t, t_1, \bar{t}) \mathbf{E}(t) \mathbf{E}(t_1) \mathbf{E}(\bar{t}), \quad (5.39)$$

respectively for the second and third order terms, where  $a$  and  $b$  index the primary space. The  $\boldsymbol{\mu}_{ab}^{(2)}$  and  $\boldsymbol{\mu}_{ab}^{(3)}$  terms are analogous to the ordinary dipole matrix elements but now given with respect to the number of nonresonant photons, and are written in their complete form as

$$\begin{aligned} \boldsymbol{\mu}_{ab}^{(2)}(t - \bar{t}) &= \frac{i}{\hbar} \langle \varphi_a | \hat{\boldsymbol{\mu}} \hat{Q} U_2^{(\text{mol})}(t - \bar{t}) \hat{Q} \hat{\boldsymbol{\mu}} | \varphi_b \rangle \\ &= \frac{i}{\hbar} \sum_x \boldsymbol{\mu}_{ax} e^{-i\hat{H}_x \tau / \hbar} \boldsymbol{\mu}_{xb} \end{aligned} \quad (5.40)$$

and

$$\begin{aligned} \boldsymbol{\mu}_{ab}^{(3)}(t, t_1, \bar{t}) &= \frac{1}{\hbar^2} \langle \varphi_a | \hat{\boldsymbol{\mu}} \hat{Q} U_2^{(\text{mol})}(t - t_1) \hat{Q} \hat{\boldsymbol{\mu}} \hat{Q} U_2^{(\text{mol})}(t_1 - \bar{t}) \hat{Q} \hat{\boldsymbol{\mu}} | \varphi_b \rangle \\ &= \frac{1}{\hbar^2} \sum_{x,y} \boldsymbol{\mu}_{ax} e^{-i\hat{H}_x(t-t_1)/\hbar} \boldsymbol{\mu}_{xy} e^{-i\hat{H}_y(t_1-\bar{t})/\hbar} \boldsymbol{\mu}_{yb} \end{aligned} \quad (5.41)$$

where the second equality in both equations is obtained by introducing an expansion with respect to the secondary electronic states and in doing so the transition dipole matrix elements, e.g.  $\boldsymbol{\mu}_{ax}$ , are introduced, where  $x$  is an index for the secondary space.

In order to account for nonresonant transitions with larger number of photons, the corresponding order of the kernel should be taken. In the rest of this work, we will consider up to the third order of the kernel, i.e. inclusion of two and three photon contributions. This results in the following effective TDSE for the primary vibrational states

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}|\chi_a(t)\rangle &= \hat{H}_a|\chi_a(t)\rangle - \mathbf{E}(t) \sum_b \boldsymbol{\mu}_{ab}|\chi_b(t)\rangle \\
&- \sum_b \int_{t_0}^t d\bar{t} \boldsymbol{\mu}_{ab}^{(2)}(t-\bar{t})\mathbf{E}(t)\mathbf{E}(\bar{t})|\chi_b(\bar{t})\rangle \\
&- \sum_b \int_{t_0}^t d\bar{t} \int_{\bar{t}}^t dt_1 \boldsymbol{\mu}_{ab}^{(3)}(t,t_1,\bar{t})\mathbf{E}(t)\mathbf{E}(t_1)\mathbf{E}(\bar{t})|\chi_b(\bar{t})\rangle,
\end{aligned} \tag{5.42}$$

where the first two terms describe the evolution of the vibrational wave function within the primary state space,  $\boldsymbol{\mu}_{ab}$  represents the transition dipole matrix elements, and  $|\chi_a\rangle$  and  $|\chi_b\rangle$  are the vibrational state located on the  $a^{\text{th}}$  and  $b^{\text{th}}$  electronic state, respectively. The last two terms are second and third order contributions which describe the possible nonresonant two- and three-photon transitions and effectively account for the secondary state space, where  $\boldsymbol{\mu}_{ab}^{(2)}(t-\bar{t})$  and  $\boldsymbol{\mu}_{ab}^{(3)}(t,t_1,\bar{t})$  are given in eqs. 5.40 and 5.41 respectively.

## 5.4 Rotating Wave Approximation

The time nonlocality that emerged from partitioning the complete space into a primary and secondary state space is removed by implementing the rotating wave approximation (RWA) to nonresonant multiphoton transitions (NMT) and applying the secondary space density of states (DOS). A reasonable approximation is also elucidated for a concrete expression of the transition matrix elements, given as integral terms for the nonresonant portion in eq. 5.42. In order to arrive at the RWA the molecular wave function is expanded with respect to powers of the basic oscillation  $\sim \exp(-i\omega t)$  of the applied pulse. Accordingly, the vibrational wave function is expanded in orders of the field frequency

and is given below

$$\chi_a(t) = \sum_n e^{-in\omega t} \chi_a(n; t), \quad (5.43)$$

where  $n$  runs over all integer values. This expansion modifies the coupled time-dependent Schrödinger eqs. 5.42 to

$$\begin{aligned} \sum_n e^{-in\omega t} \left( [i\hbar \frac{\partial}{\partial t} + n\hbar\omega - H_a] |\chi_a(n; t)\rangle \right. \\ \left. + \frac{1}{2} \sum_b \mu_{ab} [E(t) |\chi_b(n-1; t)\rangle + E^*(t) |\chi_b(n+1; t)\rangle] \right. \\ \left. - \sum_b \int_{t_0}^t d\bar{t} K_{ab}(t, \bar{t}) e^{in\omega(t-\bar{t})} |\chi_b(n; t)\rangle \right) = 0. \end{aligned} \quad (5.44)$$

Note the introduction of  $\mu_{ab} = \mathbf{n}\boldsymbol{\mu}_{ab}$  and the abbreviation for  $K_{ab}^{(2)} + K_{ab}^{(3)}$  as  $K_{ab}$ . These latter quantities also depend on the field amplitudes  $E(t)$  and  $E^*(t)$ . The RWA has been achieved if one assumes that the time dependence of the expression in the large bracket in eq. 5.44 is slow compared to the oscillations with multiples of  $\omega$ . This leads to

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\chi_a(n; t)\rangle = [n\hbar\omega - H_a] |\chi_a(n; t)\rangle \\ - \frac{1}{2} \sum_b \mu_{ab} [E(t) |\chi_b(n-1; t)\rangle + E^*(t) |\chi_b(n+1; t)\rangle] \\ + \sum_b \int_{t_0}^t d\bar{t} K_{ab}(t, \bar{t}) e^{in\omega(t-\bar{t})} |\chi_b(n; t)\rangle. \end{aligned} \quad (5.45)$$

The requirement that the time-dependence of eq. 5.45 be slow is guaranteed if a restriction to  $n$  is taken where the energy difference corresponding to  $n\hbar\omega - \epsilon_a$  is much smaller than  $\hbar\omega$ .

### 5.4.1 Revisiting the Effective Vibrational Schrödinger Equation

The effective TDSE, eq. 5.42 is reformulated in the framework of the RWA. It is accomplished by expanding the vibrational wave function with respect to the basic oscillations of the applied pulse as seen in eq. 5.43 and arranging the expression in common  $e^{-in\omega t}$  terms. This process will be conducted in two steps; first the technique will be applied to the nonresonant two-photon term followed by the nonresonant three-photon term of eq. 5.42.

### The Two-photon Term

Applying the expansion of the vibrational wave functions presented in eq. 5.43, as well as the electric field, given in eq. 5.6, to the nonresonant two-photon term of eq. 5.42 results in the following expression,

$$\begin{aligned}
 - \sum_b \int_{t_0}^t d\bar{t} \mu_{ab}^{(2)}(t - \bar{t}) \mathbf{E}(t) \mathbf{E}(\bar{t}) |\chi_b(\bar{t})\rangle &= -\frac{1}{4} \sum_n e^{-in\omega t} \sum_b \int_{t_0}^t d\bar{t} \mu_{ab}^{(2)}(t - \bar{t}) e^{in\omega t} \\
 & [E(t)e^{-i\omega t} + E^*(t)e^{i\omega t}] [E(\bar{t})e^{-i\omega\bar{t}} + E^*(\bar{t})e^{i\omega\bar{t}}] e^{-in\omega\bar{t}} |\chi_b(n; \bar{t})\rangle
 \end{aligned} \tag{5.46}$$

where  $\mu_{ab}^{(2)} = \boldsymbol{\mu}_{ab}^{(2)} \mathbf{n}\mathbf{n}$  has been introduced. An extra oscillating factor  $1 = e^{-in\omega t} e^{in\omega t}$  has also been introduced into the sum over  $n$  in order to arrange all terms with respect to a common prefactor  $e^{-in\omega t}$ . The ordering of this equation with respect to the common prefactor,  $e^{-in\omega t}$ , results in a shift of the vibrational wave function from  $|\chi_b(n; \bar{t})\rangle$  to  $|\chi_b(n \pm 2; \bar{t})\rangle$ . Introducing the time difference term,  $\tau = t - \bar{t}$  results in the following

$$- \sum_b \int_{t_0}^t d\bar{t} \mu_{ab}^{(2)}(t - \bar{t}) \mathbf{E}(t) \mathbf{E}(\bar{t}) |\chi_b(\bar{t})\rangle = -\frac{1}{4} \sum_n e^{-in\omega t} \sum_b \int_0^{t-t_0} d\tau |I_{ab}^{(2)}(n; t, \tau)\rangle, \tag{5.47}$$

where the individual terms are condensed in  $|I_{ab}^{(2)}(n; t, \tau)\rangle$  and are revealed as

$$\begin{aligned}
 |I_{ab}^{(2)}(n; t, \tau)\rangle &= \mu_{ab}^{(2)}(\tau) \\
 & \times \left( E(t)E(t - \tau)e^{i(n-1)\omega\tau} |\chi_b(n - 2; t - \tau)\rangle \right. \\
 & + E(t)E^*(t - \tau)e^{i(n-1)\omega\tau} |\chi_b(n; t - \tau)\rangle \\
 & + E^*(t)E(t - \tau)e^{i(n+1)\omega\tau} |\chi_b(n; t - \tau)\rangle \\
 & \left. + E^*(t)E^*(t - \tau)e^{i(n+1)\omega\tau} |\chi_b(n + 2; t - \tau)\rangle \right).
 \end{aligned} \tag{5.48}$$

The vibrational wavefunction's expansion coefficients, see eq. 5.43, take the values of  $n$  and  $n \pm 2$ .

### The Three-photon Term

The nonresonant three-photon term of eq. 5.42 is also expanded by applying eq. 5.43, as was done for the two-photon term previously. This results in the following expression

$$\begin{aligned}
& - \sum_b \int_{t_0}^t d\bar{t} \int_{\bar{t}}^t dt_1 \mu_{ab}^{(3)}(t, t_1, \bar{t}) \mathbf{E}(t) \mathbf{E}(t_1) \mathbf{E}(\bar{t}) |\chi_b(\bar{t})\rangle = \\
& - \frac{1}{8} \sum_n e^{-in\omega t} \sum_b \int_{t_0}^t d\bar{t} \int_{\bar{t}}^t dt_1 \mu_{ab}^{(3)}(t, t_1, \bar{t}) e^{in\omega t} [E(t)e^{-i\omega t} + E^*(t)e^{i\omega t}] \\
& [E(t_1)e^{-i\omega t_1} + E^*(t_1)e^{i\omega t_1}] [E(\bar{t})e^{-i\omega \bar{t}} + E^*(\bar{t})e^{i\omega \bar{t}}] e^{-in\omega \bar{t}} |\chi_b(n; \bar{t})\rangle,
\end{aligned} \tag{5.49}$$

where the term  $\mu_{ab}^{(3)} = \boldsymbol{\mu}_{ab}^{(3)} \mathbf{nnn}$  has been introduced. New time arguments  $t - \bar{t} = \tau$  and  $t_1 - \bar{t} = \bar{\tau}$  can be substituted into the expression. Arranging the expression again in terms of a common prefactor,  $e^{-in\omega t}$  results in the following form

$$\begin{aligned}
& - \sum_b \int_{t_0}^t d\bar{t} \int_{\bar{t}}^t dt_1 \mu_{ab}^{(3)}(t, t_1, \bar{t}) \mathbf{E}(t) \mathbf{E}(t_1) \mathbf{E}(\bar{t}) |\chi_b(\bar{t})\rangle = \\
& - \frac{1}{8} \sum_n e^{-in\omega t} \sum_b \int_0^{t-t_0} d\tau \int_0^\tau d\bar{\tau} |I_{ab}^{(3)}(n; t, \tau, \bar{\tau})\rangle,
\end{aligned} \tag{5.50}$$

where  $|I_{ab}^{(3)}\rangle$  is given below in its full complexity:

$$\begin{aligned}
|I_{ab}^{(3)}(n; t, \tau, \bar{\tau})\rangle = & \mu_{ab}^{(3)}(\tau - \bar{\tau}, \bar{\tau}) \\
& \times \left( E(t)E(t - (\tau - \bar{\tau}))E(t - \tau)e^{-i\omega\bar{\tau} + i(n-1)\omega\tau} |\chi_b(n-3; t - \tau)\rangle \right. \\
& + E(t)E^*(t - (\tau - \bar{\tau}))E(t - \tau)e^{i\omega\bar{\tau} + i(n-1)\omega\tau} |\chi_b(n-1; t - \tau)\rangle \\
& + E^*(t)E(t - (\tau - \bar{\tau}))E(t - \tau)e^{-i\omega\bar{\tau} + i(n+1)\omega\tau} |\chi_b(n-1; t - \tau)\rangle \\
& + E^*(t)E^*(t - (\tau - \bar{\tau}))E(t - \tau)e^{i\omega\bar{\tau} + i(n+1)\omega\tau} |\chi_b(n+1; t - \tau)\rangle \\
& + E(t)E(t - (\tau - \bar{\tau}))E^*(t - \tau)e^{-i\omega\bar{\tau} + i(n-1)\omega\tau} |\chi_b(n-1; t - \tau)\rangle \\
& + E(t)E^*(t - (\tau - \bar{\tau}))E^*(t - \tau)e^{i\omega\bar{\tau} + i(n-1)\omega\tau} |\chi_b(n+1; t - \tau)\rangle \\
& + E^*(t)E(t - (\tau - \bar{\tau}))E^*(t - \tau)e^{-i\omega\bar{\tau} + i(n+1)\omega\tau} |\chi_b(n+1; t - \tau)\rangle \\
& \left. + E^*(t)E^*(t - (\tau - \bar{\tau}))E^*(t - \tau)e^{i\omega\bar{\tau} + i(n+1)\omega\tau} |\chi_b(n+3; t - \tau)\rangle \right).
\end{aligned} \tag{5.51}$$

### Effective Vibrational Schrödinger Equation in Terms of RWA

The previously described two-photon and three-photon nonresonant terms have been analyzed with respect to the expansion of the vibrational wave function and to the basic oscillations of the electric field. Inserting these expressions back into the effective vibrational Schrödinger equation, equation. 5.42, results in the following,

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} |\chi_a(n; t)\rangle = & \left( (\hat{H}_a - n\hbar\omega) |\chi_a(n; t)\rangle - \frac{1}{2} \sum_b \mu_{ab} (E(t) |\chi_b(n-1; t)\rangle + E^*(t) |\chi_b(n+1; t)\rangle) \right) \\
 & - \frac{1}{4} \sum_b \int_0^{t-t_0} d\tau |I_{ab}^{(2)}(n; t, \tau)\rangle - \frac{1}{8} \sum_b \int_0^{t-t_0} d\tau \int_0^\tau d\bar{\tau} |I_{ab}^{(3)}(n; t, \tau, \bar{\tau})\rangle
 \end{aligned}
 \tag{5.52}$$

which is given in terms of the basic oscillations of the field. In order to arrive at the RWA, it must be guaranteed that the prefactor  $(\hat{H}_a - n\hbar\omega)$  is much less than  $\hbar\omega$ . Consequently, the vibrational wave function's expansion coefficients depend on  $n$ . For clarity it should be noted that in a case of a two-level system, to describe a nonresonant two-photon transition requires that  $n = 0$  and  $\pm 2$ . This corresponds to the ground electronic state and the two-photons needed to populate the excited electronic state, respectively. To describe a nonresonant three-photon transition then  $n = 0$  and  $\pm 3$ , again for the ground and excited electronic states, respectively. This selection of  $n$ , which depends on the system being studied, reduces the terms described in eqs. 5.48 and 5.51 as will be seen in the following section, when the equation is applied to a two-level system.

The time nonlocality that resulted from the use of the projection operators is removed based on the expansion of the vibrational states. The justification stems from eqs. 5.47 and 5.50, in which the electric field envelope and the expansion coefficients are all time ordered. In both equations, the time interval in  $\mu_{ab}^{(2)}$  and  $\mu_{ab}^{(3)}$  is considered to be short, at least short in comparison to the interval of the envelope and the expansion coefficients and therefore the latter two are extracted from the integrals. In addition, by applying the RWA to the equations as was done for a basal three-level system, the fast oscillating terms of the field are removed. Therefore, the local time approximation is based on the slow varying behavior of the vibrational wave function as well as the field envelope.

### Evaluation of the Transition Matrix Elements

In the following the DOS for the secondary states from equation 5.19 is reintroduced in order to investigate the dipole components of the Schrödinger equation for NMT. Upon applying the DOS to equation 5.40 the following two-photon component is obtained

$$\boldsymbol{\mu}_{ab}^{(2)}(\tau) = \frac{i}{\hbar} \int d\Omega \varrho(\Omega) \boldsymbol{\mu}(a, \Omega) e^{-i\Omega\tau} \boldsymbol{\mu}(\Omega, b), \quad (5.53)$$

and describes the frequency dependent dipole matrix elements for a transition from state  $b$  into the continuum and from the continuum to the final state  $a$ . The three-photon dipole component

$$\boldsymbol{\mu}_{ab}^{(3)}(t, t_1, \bar{t}) = \frac{1}{\hbar^2} \int d\Omega d\bar{\Omega} \varrho(\Omega) \varrho(\bar{\Omega}) \boldsymbol{\mu}(a, \Omega) e^{-i\Omega(t-t_1)} \boldsymbol{\mu}(\Omega, \bar{\Omega}) e^{-i\bar{\Omega}(t_1-\bar{t})} \boldsymbol{\mu}(\bar{\Omega}, b) \quad (5.54)$$

describes a three step transition from the an initial state  $b$  into the continuum and from the continuum to the final state  $a$  via a continuum-continuum transition. This term depends on three different time units  $t, t_1,$  and  $\bar{t}$  and to a dependence of two frequency terms  $\Omega$  and  $\bar{\Omega}$ .

Based on eq. 5.48, the multiples of the field frequency that are allowed when  $n = 0$  and  $n = 2$  are  $\nu = \pm 1$  and 3 and taking  $t_0 \rightarrow -\infty$  and defining  $\mu = \boldsymbol{\mu} \mathbf{n}$  one obtains the following set of equations

$$\begin{aligned} \int_0^{\infty} d\tau e^{i\nu\omega\tau} \boldsymbol{\mu}_{ab}^{(2)}(\tau) &= \frac{i}{\hbar} \int_0^{\infty} d\tau \int d\Omega \varrho(\Omega) e^{i(\nu\omega - \Omega)\tau} \boldsymbol{\mu}(a, \Omega) \boldsymbol{\mu}(\Omega, b) \\ &= -\frac{1}{\hbar} \int d\Omega \varrho(\Omega) \frac{\boldsymbol{\mu}(a, \Omega) \boldsymbol{\mu}(\Omega, b)}{\nu\omega - \Omega + i\epsilon}, \end{aligned} \quad (5.55)$$

where the term in the denominator comes from the time integration of the exponential term. This expression can be simplified by neglecting the frequency components  $\nu\omega$  of the laser field, which have a much smaller value than the frequency  $\Omega$  of the secondary DOS. Applying this approximation one ends up with an expression for the two-photon dipole matrix elements

$$\begin{aligned} -\frac{1}{\hbar} \int d\Omega \varrho(\Omega) \frac{\boldsymbol{\mu}(a, \Omega) \boldsymbol{\mu}(\Omega, b)}{\nu\omega - \Omega + i\epsilon} &\approx \frac{1}{\hbar} \int d\Omega \frac{\varrho(\Omega)}{\Omega} \boldsymbol{\mu}(a, \Omega) \boldsymbol{\mu}(\Omega, b) \\ &\equiv \boldsymbol{\mu}_{ab}^{(2)} \approx \frac{\bar{\varrho}}{\hbar} \boldsymbol{\mu}_{\text{eff}}^2, \end{aligned} \quad (5.56)$$



where  $\bar{\varrho} = \int d\omega \frac{\varrho(\Omega)}{\Omega}$  is the mean DOS for the secondary states, and  $\mu_{\text{eff}}$  is the mean transition dipole moment from one of the two primary states into the manifold of secondary states. In order to arrive at a similar expression for the double integration term corresponding to a three-photon transition, the same steps are applied as were done for the approximate value of  $\mu_{ab}^{(2)}$ . Starting with the given expression

$$\begin{aligned}
& \int_0^\infty d\tau \int_0^\tau d\bar{\tau} \mu_{ef}^{(3)}(\tau - \bar{\tau}, \bar{\tau}) e^{i\gamma\omega\tau + i\nu\omega\bar{\tau}} \\
&= -\frac{1}{\hbar^2} \int_0^\infty d\tau \int_0^\tau d\bar{\tau} \int d\Omega d\bar{\Omega} \varrho(\Omega) \varrho(\bar{\Omega}) e^{i(\gamma\omega - \Omega)\tau + i(\nu\omega + \Omega - \bar{\Omega})\bar{\tau}} \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f) \\
&= -\frac{1}{\hbar^2} \int_0^\infty d\tau \int d\Omega d\bar{\Omega} \varrho(\Omega) \varrho(\bar{\Omega}) \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f) e^{i(\gamma\omega - \Omega)\tau} \frac{e^{i(\nu\omega + \Omega - \bar{\Omega})\tau} - 1}{i(\nu\omega + \Omega - \bar{\Omega})} \\
&= -\frac{1}{\hbar^2} \int d\Omega d\bar{\Omega} \frac{\varrho(\Omega) \varrho(\bar{\Omega}) \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f)}{\nu\omega + \Omega - \bar{\Omega}} \left( \frac{1}{(\gamma + \nu)\omega - \bar{\Omega} + i\epsilon} - \frac{1}{\gamma\omega - \bar{\Omega} + i\epsilon} \right), \tag{5.57}
\end{aligned}$$

the integration over time has been carried out twice and results in the denominator terms. The frequency of  $\Omega$  and the mean value of the frequency  $\bar{\Omega}$  for the DOS are considered to be much larger in value than the frequency components  $\nu\omega$  and  $\gamma\omega$  and therefore the latter are neglected, resulting in the following expression

$$\begin{aligned}
& -\frac{1}{\hbar^2} \int d\Omega d\bar{\Omega} \frac{\varrho(\Omega) \varrho(\bar{\Omega}) \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f)}{\nu\omega + \Omega - \bar{\Omega}} \left( \frac{1}{(\gamma + \nu)\omega - \bar{\Omega} + i\epsilon} - \frac{1}{\gamma\omega - \bar{\Omega} + i\epsilon} \right) \\
& \approx \frac{1}{\hbar^2} \int d\Omega d\bar{\Omega} \frac{\varrho(\Omega) \varrho(\bar{\Omega}) \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f)}{\nu\omega + \Omega - \bar{\Omega}} \frac{\Omega - \bar{\Omega}}{\Omega \bar{\Omega}} \\
& \approx \frac{1}{\hbar^2} \int d\Omega d\bar{\Omega} \frac{\varrho(\Omega) \varrho(\bar{\Omega}) \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f)}{\Omega \bar{\Omega}}, \tag{5.58}
\end{aligned}$$

where the common  $\Omega - \bar{\Omega}$  on the numerator and denominator cancel. The final set of expressions given below,

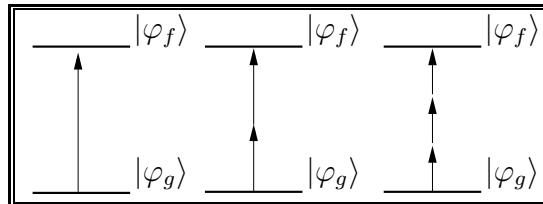
$$\begin{aligned}
& \frac{1}{\hbar^2} \int d\Omega d\bar{\Omega} \frac{\varrho(\Omega) \varrho(\bar{\Omega}) \mu(e, \Omega) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f)}{\Omega \bar{\Omega}} \\
&= \frac{1}{\hbar} \int d\Omega \frac{\varrho(\Omega) \mu(e, \Omega)}{\Omega} \frac{1}{\hbar} \int d\bar{\Omega} \frac{\varrho(\bar{\Omega}) \mu(\Omega, \bar{\Omega}) \mu(\bar{\Omega}, f)}{\bar{\Omega}} \tag{5.59} \\
&\equiv \mu_{ef}^{(3)} \approx \frac{\bar{\varrho}^2}{\hbar^2} \mu_{\text{eff}}^3
\end{aligned}$$

accounts for a single dipole matrix element from the left integration and a squared dipole matrix element from the right integration. The final expression is defined in terms of the mean value of the DOS  $\bar{\rho}$  for the secondary states and the transition dipole moment  $\mu_{\text{eff}}$ . Considering the transition dipole matrix elements between the primary states and the secondary states to be similar to the transition dipole matrix elements occurring between the secondary electronic states is a rather crude approximation. However, because it is not yet known how to calculate these values, eq. 5.59 provides a suitable parametrization of the effective transition matrix elements.

### 5.4.2 A Two-level System

In the previous section 5.4.3 the reasoning behind moving from a time nonlocal to a time local term was explained via the expansion of vibrational coefficients and eventually the use of the RWA. It was also shown that the transition matrix elements can be approximated by introducing the DOS for the secondary states. Because the model is being developed step by step, a two-level system is introduced in which a resonant one-, nonresonant two- and three-photon transitions will be explored as can be seen in fig. 5.2.

**Figure 5.2:** The scheme for the rudimentary two-level system from which resonant single-, nonresonant two-, and three-photon transitions are explored.



#### Resonant One-Photon Transitions

The resonant one-photon transition process is used here for purposes of comparison and will be used to exemplify our approach for NMT. Solving the Schrödinger equation for a two-level system one obtains the following equations of motion for the ground

$$i\hbar \frac{\partial}{\partial t} |\chi_g(0; t)\rangle = \hat{H}_g |\chi_g(0; t)\rangle - \frac{1}{2} \mu_{gf} E^*(t) |\chi_f(1; t)\rangle, \quad (5.60)$$

and excited

$$i\hbar \frac{\partial}{\partial t} |\chi_f(1; t)\rangle = (\hat{H}_f - \hbar\omega) |\chi_f(1; t)\rangle - \frac{1}{2} \mu_{fg} E(t) |\chi_g(0; t)\rangle \quad (5.61)$$

vibrational wave functions within the scope of the RWA, i.e. where  $n = 0$  and  $n = 1$  for the ground and final vibrational wave functions, respectively. The rotational wave Hamiltonian is written as

$$\hat{\mathbf{H}}^{(\text{RWA})}(t) = \hat{\mathbf{H}}_{\text{mol}}^{(\text{RWA})} + \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t) \quad (5.62)$$

where the molecular Hamiltonian is defined as

$$\hat{\mathbf{H}}_{\text{mol}}^{(\text{RWA})} = \hat{H}_g |\varphi_g\rangle \langle \varphi_g| + (\hat{H}_f - \hbar\omega) |\varphi_f\rangle \langle \varphi_f|. \quad (5.63)$$

The field Hamiltonian has the following form

$$\hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t) = -\frac{1}{2}E(t)\mu_{fg}|\varphi_f\rangle\langle\varphi_g| - \frac{1}{2}E^*(t)\mu_{gf}|\varphi_g\rangle\langle\varphi_f| \quad (5.64)$$

where the fast oscillations of the electric field have been removed leaving the field envelope and the transition matrix elements  $\mu_{fg}$  and  $\mu_{gf}$ , or rather traditionally the transition dipole matrix elements.

### Nonresonant Two-photon Transitions

The equations of motion for nonresonant two-photon transitions are obtained according to eq. 5.52 and the approximations that followed. Given below are the ground

$$i\hbar\frac{\partial}{\partial t}|\chi_g(0;t)\rangle = \hat{H}_g|\chi_g(0;t)\rangle - \frac{1}{2}\mu_{gg}^{(2)}|E(t)|^2|\chi_g(0;t)\rangle - \frac{1}{4}\mu_{gf}^{(2)}E^{*2}(t)|\chi_f(2;t)\rangle \quad (5.65)$$

and excited

$$i\hbar\frac{\partial}{\partial t}|\chi_f(2;t)\rangle = (\hat{H}_f - 2\hbar\omega)|\chi_f(2;t)\rangle - \frac{1}{2}\mu_{ff}^{(2)}|E(t)|^2|\chi_f(2;t)\rangle - \frac{1}{4}\mu_{fg}^{(2)}E^2(t)|\chi_g(0;t)\rangle \quad (5.66)$$

vibrational wave functions defined by the second order of the field envelope  $E(t)$ . The equations were obtained by applying the RWA, where  $n = 0$  and  $n = 2$  for the ground and final states respectively. The applied nonresonant two-photon molecular Hamiltonian is defined below

$$\hat{\mathbf{H}}_{\text{mol}}^{(\text{RWA}-2)} = \hat{H}_g |\varphi_g\rangle \langle \varphi_g| + (\hat{H}_f - 2\hbar\omega) |\varphi_f\rangle \langle \varphi_f|. \quad (5.67)$$

The transition matrix elements  $\mu_{gf}^{(2)}$  and  $\mu_{fg}^{(2)}$  are given in eq. 5.56. The effective molecular field coupling Hamiltonian for the RWA description reads,

$$\hat{\mathbf{H}}_{\text{field}}^{(\text{RWA}-2)}(t) = -\frac{1}{2}\sum_{a=g,f}|E(t)|^2\mu_{aa}^{(2)}|\varphi_a\rangle\langle\varphi_a| - \frac{1}{4}E^2(t)\mu_{fg}^{(2)}|\varphi_f\rangle\langle\varphi_g| - \frac{1}{4}E^{*2}(t)\mu_{gf}^{(2)}|\varphi_g\rangle\langle\varphi_f| \quad (5.68)$$

where the first term describes the contribution of the permanent dipole moments for both states, and the remaining terms describe the transition between the ground state and the final excited state.

### Nonresonant Three-photon Transitions

The last considered scenario within the two-level system is the interaction between two electronic states via a nonresonant three-photon mechanism. The equations of motions for the ground vibrational wave function

$$i\hbar\frac{\partial}{\partial t}|\chi_g(0;t)\rangle = \hat{H}_g|\chi_g(0;t)\rangle - \frac{1}{8}\mu_{gf}^{(3)}E^{*3}(t)|\chi_f(3;t)\rangle \quad (5.69)$$

and the excited state vibrational wave function

$$i\hbar\frac{\partial}{\partial t}|\chi_f(3;t)\rangle = (\hat{H}_f - 3\hbar\omega)|\chi_f(3;t)\rangle - \frac{1}{8}\mu_{fg}^{(3)}E^3(t)|\chi_g(0;t)\rangle. \quad (5.70)$$

are given with respect to the values  $n = 0$  and  $n = 3$  respectively. The molecular Hamiltonian for a nonresonant three-photon transition is defined as

$$\hat{H}_{\text{mol}}^{(\text{RWA}-3)} = \hat{H}_g|\varphi_g\rangle\langle\varphi_g| + (\hat{H}_f - 3\hbar\omega)|\varphi_f\rangle\langle\varphi_f|. \quad (5.71)$$

The fast oscillating terms of the laser field are neglected again as can be seen from the molecular field Hamiltonian. The molecular field Hamiltonian is now defined as

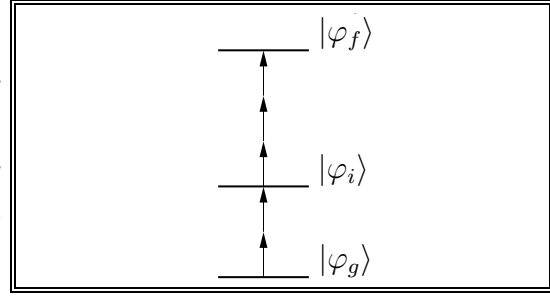
$$\hat{H}_{\text{field}}^{(\text{RWA}-3)}(t) = -\frac{1}{8}E^3(t)\mu_{fg}^{(3)}|\varphi_f\rangle\langle\varphi_g| - \frac{1}{8}E^{*3}(t)\mu_{gf}^{(3)}|\varphi_g\rangle\langle\varphi_f| \quad (5.72)$$

in terms of the field envelope. The transition matrix elements  $\mu_{gf}^{(3)}$  and  $\mu_{fg}^{(3)}$  are given in eq. 5.59.

### 5.4.3 A Three-level System

Two nonresonant processes are described in eq. 5.52. Considering a system which accounts for both types of nonresonant transitions leads to a basal three-level system. Two possibilities arise; one in which the first transition occurs via two and the second transition via three photons, or vice versa, as depicted in figure 5.3. The former of the two will be investigated via the equations of motion where the three electronic states are denoted

**Figure 5.3:** A basal system which accounts for nonresonant two and three-photon transitions. The first a two-photon followed by a three-photon transition.



by  $a = g, i, f$ . These equations couple the ground state to the intermediate excited state via a two-photon transition,  $|\varphi_g\rangle \xrightarrow{2\hbar\omega} |\varphi_i\rangle$  and the intermediate excited state is coupled to the final excited state via a three-photon transition,  $|\varphi_i\rangle \xrightarrow{3\hbar\omega} |\varphi_f\rangle$ . The application of the RWA description to the equations of motion, corresponds to the oscillations which contribute multiples of 0, 2, and 5 to  $\exp(\pm i\omega t)$ . The other multiplies are completely neglected. This corresponds to the vibrational expansion coefficients  $|\chi_g(0; t)\rangle$ ,  $|\chi_i(2; t)\rangle$ , and  $|\chi_f(5; t)\rangle$ , i.e. where  $n = 0, 2$  and 5. This scenario relates to the RWA for eq. 5.52 and is obtained by eliminating all multiples of  $\hbar\omega$  which do not correspond to the Schrödinger equation being evaluated. The neglect of these terms guarantees that any oscillation with multiples of  $\hbar\omega$  are absent in the remaining expansion coefficients, including single photon transitions. This is best understood when writing out the equations of motion for each time local vibrational state. Starting with the ground state vibrational wave function, its evolution is defined by the following

$$i\hbar \frac{\partial}{\partial t} |\chi_g(0; t)\rangle = \hat{H}_g |\chi_g(0; t)\rangle - \frac{1}{4} \mu_{gg}^{(2)} |E(t)|^2 |\chi_g(0; t)\rangle - \frac{1}{4} \mu_{gi}^{(2)} E^{*2}(t) |\chi_i(2; t)\rangle \quad (5.73)$$

where  $n = 0$ . The excited vibrational state includes only those coefficients that carry the value  $n = 2$ , the other terms are neglected. The equation of motion for the excited state vibrational wave function, where  $n = 2$ , reads

$$i\hbar \frac{\partial}{\partial t} |\chi_i(2; t)\rangle = (\hat{H}_i - 2\hbar\omega) |\chi_i(2; t)\rangle - \frac{1}{4} \mu_{ii}^{(2)} |E(t)|^2 |\chi_i(2; t)\rangle - \frac{1}{4} \mu_{ig}^{(2)} E^2(t) |\chi_g(0; t)\rangle - \frac{1}{8} \mu_{if}^{(2)} E^{*3}(t) |\chi_f(5; t)\rangle \quad (5.74)$$

which is influenced by the expansion coefficients for the intermediate and final excited states, as can be seen from eqs. 5.48 and 5.51 in which only the  $n$  values of 2 and 5 are allowed. The first term is responsible for removing the resonant two-photon energy from the intermediate state, essentially shifting the intermediate state to the energetic region of the ground state. Finally, the wave function belonging to the final excited state obeys

$$i\hbar \frac{\partial}{\partial t} |\chi_f(5; t)\rangle = (\hat{H}_f - 5\hbar\omega) |\chi_f(5; t)\rangle - \frac{1}{8} \mu_{fi}^{(3)} E^3(t) |\chi_i(2; t)\rangle \quad (5.75)$$

which is influenced only by the expansion coefficients from the excited vibrational expansion coefficients,  $|\chi_i(2, t)\rangle$ . The final state molecular Hamiltonian  $\hat{H}_f$  is shifted by five photons of energy which corresponds to a resonance between the final state and the ground state.

## 5.5 Formulation of OCT for NMT

The standard version of optimal control theory was presented in section 4.2.1 which included in the functional, equation 4.1, the complete electric field. In this section OCT will be developed in terms of the RWA for NMT processes. The corresponding functional is given as

$$J(t_f; E, E^*) = |\langle \Psi_{\text{tar}} | \Psi(t_f) \rangle|^2 - \lambda \int_{t_0}^{t_f} dt |E(t)|^2 \quad (5.76)$$

where all multiples of the carrier frequency  $\omega$  are neglected. The functional then only depends on the field envelope as well as its complex conjugate. The control task will optimize the field envelope  $E(t)$  rather than the complete electric field  $\mathbf{E}(t)$  and any modulation that would normally occur in the complete electric field formulation will also be accounted for in the field envelope  $E(t)$ . The optimal pulse can then be calculated by inserting the optimized envelope into eq. 5.6.

The control yield, see eq. 4.2, upon calculation of the optimal field, is rarely equal to one, and depends on the allowed field strengths. The iterative scheme of ref. [102, 129, 130] as applied in this work is valid for all field strengths. Limiting the field intensity to the weak field regime drastically reduces the control yield to a value much less than one. It is therefore of interest to quantify the amount of the driven wavepacket that has reached the position of the target wavepacket. This can be measured as the renormalization of the control yield and is defined as

$$q = \frac{|\langle \chi_f^{(\text{tar})} | \chi_f(t_f) \rangle|^2}{\langle \chi_f(t_f) | \chi_f(t_f) \rangle}, \quad (5.77)$$

for a vibrational target state located on the excited electronic state,  $|\chi_f^{(\text{tar})}\rangle$ .

In order to derive an expression for the control field, the extremum of the functional  $J(t_f; E, E^*)$  is determined by applying a functional derivative with respect to the conju-

gate of the electric field envelope  $E^*(t)$ . The functional derivative of the first term in eq. 4.1, yields the following

$$\begin{aligned} \frac{\delta}{\delta E^*(t)} |\langle \Psi_{\text{tar}} | \Psi(t_f) \rangle|^2 &= \langle \Psi_{\text{tar}} | \frac{\delta U(t_f, t_0)}{\delta E^*(t)} | \Psi(t_0) \rangle \langle \Psi(t_f) | \Psi_{\text{tar}} \rangle \\ &+ \langle \Psi_{\text{tar}} | \Psi(t_f) \rangle \langle \Psi(t_0) | \left( \frac{\delta U(t_f, t_0)}{\delta E(t)} \right)^\dagger | \Psi_{\text{tar}} \rangle, \end{aligned} \quad (5.78)$$

in view of the time evolution operator  $U(t_f, t_0)$  which depends on the complex value of the field envelope. These two terms appear due to the application of the product rule. The form of the time evolution operator is given below

$$U(t_f, t_0) = \hat{T} \exp \left( - \frac{i}{\hbar} \int_{t_0}^{t_f} d\tau [\hat{\mathbf{H}}_{\text{mol}}^{(\text{RWA})} + \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(\tau)] \right). \quad (5.79)$$

where  $\hat{T}$  is the time ordering operator. Calculation of the functional derivative of eq. 5.79 results in the following

$$\frac{\delta U(t_f, t_0)}{\delta E^*(t)} = - \frac{i}{\hbar} U(t_f, t) \frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E^*(t)} U(t, t_0) \quad (5.80)$$

where the derivation has employed the following relation

$$\frac{\delta}{\delta E^*(t)} \int_{t_0}^{t_f} d\tau \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(\tau) = \frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E^*(t)} \quad (5.81)$$

with the assumption that  $t_0 < t < t_f$ . Inserting equation 5.80 into eq. 5.78 and setting the latter equal to zero, the general solution of the optimized laser envelope is obtained.

$$\begin{aligned} E(t) &= - \frac{i}{\hbar \lambda} \left[ \langle \Psi(t_f) | \Psi_{\text{tar}} \rangle \langle \Theta(t) | \frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E^*(t)} | \Psi(t) \rangle \right. \\ &\quad \left. - \langle \Psi(t) | \left( \frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E(t)} \right)^\dagger | \Theta(t) \rangle \langle \Psi_{\text{tar}} | \Psi(t_f) \rangle \right] \end{aligned} \quad (5.82)$$

The effect of the time evolution operator acting on the target state  $U(t, t_f) | \Psi_{\text{tar}} \rangle$  is an evolution backward in time, denoted as  $|\Theta(t)\rangle$ , and the effect of the operator on the initial state  $U(t, t_0) | \Psi(t_0) \rangle$  is a propagation forward in time, denoted as  $|\Psi(t)\rangle$ .

### 5.5.1 The Two-level System

The concepts, namely the equations of motion, for a rudimentary two-level system discussed in section 5.4.2 will be applied here within OCT. The structure remains consistent

beginning with the derivation of the optimal electric field envelope for a resonant one-, nonresonant two- and three-photon transitions.

### Resonant One-photon Transition

A resonant one-photon transition from the ground electronic state to the final excited state is standard and is given here for comparison to the nonresonant cases. According to eq. 5.82, the derivation of the molecular field Hamiltonian  $\hat{\mathbf{H}}_{\text{mol}}^{(\text{RWA})}$  must be performed to obtain an expression for the coupled electric field. The derivative with respect to the complex electric field envelope is given below

$$\frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E^*(t)} = -\frac{1}{2} \mu_{gf} |\varphi_g\rangle \langle \varphi_f|, \quad (5.83)$$

as well as that with respect to the electric field envelope

$$\frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E(t)} = -\frac{1}{2} \mu_{gf} |\varphi_g\rangle \langle \varphi_f| \quad (5.84)$$

Inserting eqs. 5.83 and 5.84 into eq. 5.82 results in the following expression for the control field.

$$E(t) = \frac{i\mu_{fg}}{2\hbar\lambda} \left[ \left( \langle \chi_f(t_f) | \chi_f^{\text{tar}} \rangle + \langle \chi_g(t_f) | \chi_g^{\text{tar}} \rangle \right) \langle \vartheta_g(t) | \chi_f(t) \rangle - \langle \chi_g(t) | \vartheta_f(t) \rangle \left( \langle \chi_g^{\text{tar}} | \chi_g(t_f) \rangle + \langle \chi_f^{\text{tar}} | \chi_f(t_f) \rangle \right) \right] \quad (5.85)$$

The optimal field is calculated iteratively by solving the TDSE according to eqs. 5.60 and 5.61, for the forward  $|\chi_a(t)\rangle$  and backward  $|\vartheta_a(t)\rangle$  propagated vibrational wave functions. The newly appearing  $|\vartheta_a(t_f)\rangle$  denotes the backward propagated vibrational wave function given as

$$|\vartheta(t)_a\rangle = U(t, t_f) |\chi_a^{\text{tar}}\rangle, \quad (5.86)$$

where  $U(t, t_f)$  evolves  $|\chi_a^{\text{tar}}\rangle$  backwards in time.

### Nonresonant Two-photon Transitions

The development of OCT with respect to nonresonant two-photon interactions is accomplished by first solving the derivatives for the corresponding molecular field Hamiltonian.



The solution to these derivatives are given below, first with respect to the complex conjugate of the field envelope

$$\frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E^*(t)} = -\frac{1}{2} \sum_{a=g,f} E(t) \mu_{aa}^{(2)} |\varphi_a\rangle \langle \varphi_a| - \frac{1}{2} E^*(t) \mu_{gf}^{(2)} |\varphi_g\rangle \langle \varphi_f|, \quad (5.87)$$

and second with respect to the ordinary field envelope

$$\frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E(t)} = -\frac{1}{2} \sum_{a=g,f} E^*(t) \mu_{aa}^{(2)} |\varphi_a\rangle \langle \varphi_a| - \frac{1}{2} E(t) \mu_{fg}^{(2)} |\varphi_f\rangle \langle \varphi_g|. \quad (5.88)$$

Inserting the solution to the derivatives, eqs. 5.87 and 5.88, into the expression for the control field, eq. 5.82, results in the following expression for the field envelope

$$\begin{aligned} E(t) = \frac{i}{2\hbar\lambda^{(2)}} & \left[ \left( \sum_{a=g,f} \langle \chi_a^{\text{tar}} | \chi_a(t_f) \rangle \right) \left( \sum_{a=g,f} \mu_{aa}^{(2)} \langle \vartheta_a(t) | \chi_a(t) \rangle E(t) + \mu_{gf}^{(2)} \langle \vartheta_g(t) | \chi_e(t) \rangle E^*(t) \right) \right. \\ & \left. - \left( \sum_{a=g,f} \mu_{aa}^{(2)} \langle \chi_a(t) | \vartheta_a(t) \rangle E(t) + \mu_{gf}^{(2)} \langle \chi_g(t) | \vartheta_e(t) \rangle E^*(t) \right) \left( \sum_{a=g,f} \langle \chi_a^{\text{tar}} | \chi_a(t_f) \rangle \right) \right] \end{aligned} \quad (5.89)$$

which shows an explicit dependence on the field envelope on the right-hand side of the equation. It is therefore necessary to modify the standard scheme in which the optimal field is calculated. The time-dependent Schrödinger equation for the vibrational wave functions are given by equations 5.65 and 5.66 as well as for the respective backward propagation.

The procedure to compute the optimal field can be put into a more efficient form if  $\int_{t_0}^{t_f} dt |E(t)|^2$  is replaced in eq. 5.76 by the expression  $\int_{t_0}^{t_f} dt |E(t)|^4/2$ . Then, the functional derivative with respect to  $E^*(t)$  leads to the expression  $E^*(t)E^2(t)$  instead of  $E(t)$ , on the right-hand side of equation. 5.89. Since the terms proportional to  $\mu_{aa}^{(2)}$  only result in minor corrections they are neglected and the effective control field is given as

$$\begin{aligned} \mathcal{E}(t) = \frac{i\mu_{gf}^{(2)}}{2\hbar\lambda^{(2)}} & \left[ \left( \langle \chi_f(t_f) | \chi_f^{\text{tar}} \rangle + \langle \chi_g(t_f) | \chi_g^{\text{tar}} \rangle \right) \langle \vartheta_g(t) | \chi_f(t) \rangle \right. \\ & \left. - \langle \chi_g(t) | \vartheta_f(t) \rangle \left( \langle \chi_g^{\text{tar}} | \chi_g(t_f) \rangle + \langle \chi_f^{\text{tar}} | \chi_f(t_f) \rangle \right) \right] \end{aligned} \quad (5.90)$$

where  $\mathcal{E}(t) = E^2(t)$ . Such a replacement is also possible in the related time-dependent Schrödinger eqs. 5.65 and 5.66 and the determination of the optimal field can be done in the standard way but with the primary focus on  $\mathcal{E}(t)$ .

### Nonresonant Three-photon Transitions

The last multiphoton transition that is considered is the three-photon interaction in which the molecular field Hamiltonian was given previously in eq. 5.72. In order to acquire an expression for the control field, its derivative is taken twice: once with respect to the complex electric field envelope

$$\frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E^*(t)} = -\frac{3}{8} E^{*2}(t) \mu_{gf}^{(3)} |\varphi_g\rangle \langle \varphi_f|, \quad (5.91)$$

and once with respect to the original field envelope

$$\frac{\partial \hat{\mathbf{H}}_{\text{field}}^{(\text{RWA})}(t)}{\partial E(t)} = -\frac{3}{8} E^2(t) \mu_{fg}^{(3)} |\varphi_f\rangle \langle \varphi_g|. \quad (5.92)$$

These equations are substituted into the general control field eq. 5.82 and lead to the following control field

$$E(t) = \frac{3i\mu_{gf}^{(3)} E^{*2}(t)}{8\hbar\lambda^{(3)}} \left[ (\langle \chi_f(t_f) | \chi_f^{\text{tar}} \rangle + \langle \chi_g(t_f) | \chi_g^{\text{tar}} \rangle) \langle \vartheta_g(t) | \chi_f(t) \rangle - \langle \chi_g(t) | \vartheta_f(t) \rangle (\langle \chi_g^{\text{tar}} | \chi_g(t_f) \rangle + \langle \chi_f^{\text{tar}} | \chi_f(t_f) \rangle) \right], \quad (5.93)$$

given in terms of nonresonant three-photon interactions. The time-dependent Schrödinger equations for the vibrational wave functions are given by eqs. 5.69 and 5.70 as well as for the respective versions for backward propagation.

Again, the procedure to compute the optimal field can be put into a more efficient form by replacing  $\int_{t_0}^{t_f} dt |E(t)|^2$  in eq. 5.76 with  $\int_{t_0}^{t_f} dt |E(t)|^6/3$ . Then, the functional derivative with respect to  $E^*(t)$  leads to  $E^{*2}(t)E^3(t)$  instead of  $E(t)$  on the right-hand side of equation. 5.93 and we arrive at

$$\tilde{\mathcal{E}}(t) = \frac{3i\mu_{ge}^{(3)}}{8\hbar\lambda^{(3)}} \left[ (\langle \chi_f(t_f) | \chi_f^{\text{tar}} \rangle + \langle \chi_g(t_f) | \chi_g^{\text{tar}} \rangle) \langle \vartheta_g(t) | \chi_f(t) \rangle - \langle \chi_g(t) | \vartheta_f(t) \rangle (\langle \chi_g^{\text{tar}} | \chi_g(t_f) \rangle + \langle \chi_f^{\text{tar}} | \chi_f(t_f) \rangle) \right], \quad (5.94)$$

where  $\tilde{\mathcal{E}}(t) = E^3(t)$ . Such a replacement is also possible in the related time-dependent Schrödinger eqs. 5.69 and 5.70 and the determination of the optimal field can be done in the standard way but focusing primarily on  $\tilde{\mathcal{E}}(t)$ .