

# A critical comparison of two gauges in atom-radiation interaction associated with Quantum Coherent Control

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## Abstract

In approximated treatments of atom-radiation interaction (ARI), the controversy over whether to use a velocity form (as obtained from the Coulomb gauge) or a length form (as obtained from the Multipolar gauge) was resolved by Kobe in 1979 for identical-particle systems on the basis of gauge invariance. In quantum coherent control of different-particle systems, it is still an issue of which form to choose. Although the validity of the Multipolar gauge treatment with the electric dipole approximation (EDA) is controversial, it is a proper treatment. This paper shows that, for a three-atom system, the transition rate between quantum states induced by the electromagnetic field is the same for the two forms in a resonant case with a local Hamiltonian. The paper also shows that there is a transition rate difference between the two gauges for nonlocal Hamiltonians. Reasons for a preference to the length form over the velocity form will be explained based on gauge-invariant property of the approximate molecular Hamiltonian.

## I. INTRODUCTION

Both theoretical and experimental work have shown great interest in Dynamics of reactive chemical systems. A step beyond the passive study by probing the chemical reactions, is to influence a chemical reaction to produce a desired outcome. With the emergence of the laser, which is now a very common experimental tool, many scientists desire to use optical means to control chemical reactions. Among many chemical reactions, the bimolecular chemical reaction is one of the most basic. A variety of means to control the bimolecular chemical reaction have been developed. In 1988 Krause, Shapiro and Brumer[1] advocated, the use of the phase coherence of a laser, to achieve selectivity with weak lasers, is more promising than those with a high power laser. For a bimolecular system, the initial system is subjected to a laser pulse, creating a coherent superposition of several bound levels of the electronically excited complex. After a variable delay, a second pulse photodissociates the system to the ground state continuum. In coherent control, quantum effects are used to either constructively or destructively alter product properties. “Active control results, because the excitation process explicitly imparts experimentally controllable phase and amplitude information to the molecule”, said Shapiro and Brumer.

For the atom-radiation interaction (ARI) of quantum coherent control of a bimolecular rearrangement collision for a three-atom system, a multi-dimensional Hamiltonian is constructed, which is difficult to solve exactly. In order to simplify the Hamiltonian, one could choose to use a gauge transformation. Different gauges give different Hamiltonians, but they are equally meaningful. What is more, the measurable quantities, such as expectation values, transition probabilities, and cross sections, will be identical if the exact eigenfunctions for the Hamiltonian are solved without any assumptions or approximations. However, the N-particle problem is difficult to solve exactly. In order to get reasonable results with limited calculational resources, one needs to make approximations, which may cause the result to be gauge dependent. That means the gauge dependent result may be good or bad depending on the gauge used. Most physicists, especially experimentalists, use the Coulomb gauge to treat the atom-radiation interaction. However, as shown previously by Kobe and as we demonstrate here, this is not the gauge to use for approximated treatments.

In 1945, Chandrasekhar[2] showed that when exact wavefunctions are used without approximations to the Hamiltonian, different gauge forms of oscillator strengths for electric

dipole transitions in an atomic system could be equivalently applied. The three forms: dipole length form, dipole velocity form, and dipole acceleration form can be used interchangeably. However with any Hamiltonian approximation, which form is appropriate to use has been controversial.

Many “rules of thumb” have been developed[3, 4] in consideration of quantitative calculation and qualitative analysis. In 1978, a clever and subtle way to choose between the two forms was suggested by Donald Kobe[5], by using the gauge invariance perspective to look into this problem.

Though Kobe’s conclusion was general[5, 6], the approximations and conditions he used were based on identical-particle systems for a resonant case. When quantum coherent control problem is dealt with, there are different atoms, and the Hartree-Fock method is not sufficiently accurate. The long-wavelength approximation (LWA) and other approximations will also be different from Kobe’s derivation if the system is composed of different particles.

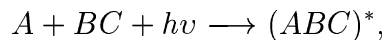
In this paper, I will compare the quantum transition rates induced by the electromagnetic field between the velocity form and length form in a quantum coherent control case. I will prove that the results are the same for both forms for local resonant cases, while they differ for nonlocal resonant cases. Finally I will test the gauge invariant features of the Hamiltonian for both forms, and argue that the length form should be used in ARI of quantum coherent control on the basis of gauge invariance.

## II. ATOM-RADIATION INTERACTION IN A THREE-ATOM SYSTEM

In order to start the discussion of the two gauges used in ARI for coherent control, some background theories of quantum coherent control and atom-radiation interaction will be addressed here.

Consider a system, composed of 3 atoms  $A, B, C$ , which is used in the bimolecular coherent control scheme proposed by Krause, Brumer and Shapiro[1]. The whole process can be broken into three parts:

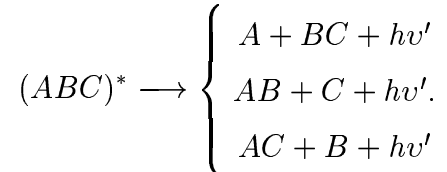
1. **Pump stage:** The three body photo-assisted recombination, which can be expressed as:



where the  $(ABC)^*$  is the coherent superposition of weakly bound vibrational-rotational states, in an excited electronic state.

2. **Evolution stage:** The time evolution of the above product.

3. **Dump stage:** Photodissociation, which can be expressed as:



In the first stage, a laser will be used to vertically pump the system to a coherent superposition of excited states. In the third stage, a second laser beam will be used to dump the system to a specific vibrational rotational state in the ground electronic state.

For the process  $\psi_1 \xrightleftharpoons{\text{pumping}} \psi_2 \xrightleftharpoons{\text{dumping}} \psi_3$  stated above, it is reasonable to divide the process into these two major atom-laser interactions. Here  $\psi_1$  is the initial ground continuum state,  $\psi_2$  is the bound excited state, and  $\psi_3$  is the final continuum state. Given two different laser beams for pumping and dumping, one has to consider the effect of both of the lasers on the Hamiltonian at different stages. Under this condition, if any gauge is applied, it is hard to transform both laser fields properly at the same time. However, one can choose to let  $\psi_2$  evolve for a long enough time that the two laser beams can be treated separately. Therefore, the dumping part can be treated in an analogous way. Hence, only the pumping stage will be considered in this paper for simplicity. At the end of the pumping pulse, the system goes into the 2nd stage, the evolution stage. The system will be given enough time to evolve before the dumping laser pulse is imposed, so that the dumping laser will not interfere with the pumping laser. At time  $t_e \gg 2\tau_p$ , where  $t_e$  is the evolution time and  $\tau_p$  is the pumping time, the pumping and the dumping processes can be treated as independent of each other as stated above.

It needs to be specified that, because  $\tau_p$  can be chosen as an experimental parameter, a vertical excitation can be used in the calculation as opposed to solving an inhomogeneous Time Dependent Schrödinger Equation (TDSE). More information can be found in Shapiro *et al.*'s paper [1]. For simplicity of derivation, I choose to start from the Hamiltonian in TDSE without any approximation.

The response of the system to the pulse can be simply written as

$$\psi_2 = \psi_1 \exp\left(\frac{-E_i t}{\hbar}\right) + \sum_j c_j \phi_j \exp\left(\frac{-E_j t}{\hbar}\right), \quad (1)$$

where  $E_i$  is the initial ground energy,  $E_j$  is the excited bound energy,  $\phi_j$  is the excited bound state wavefunction,  $c_j$  is the relevant coefficients, and  $|c_j|^2$  is the probability factor of excitation into state  $j$ .

In order to get  $c_j$ , one can apply the first order time dependent perturbation theory:

$$c_j = \frac{1}{i\hbar} \int_0^t dt \exp[i(E_j - E_1)t/\hbar] H_{j1} \quad (2)$$

Where

$$H_{j1} = \langle \psi_1 | \hat{H}_{interaction} | \phi_j \rangle. \quad (3)$$

### III. GAUGE PREPARATION IN ARI

Before any gauge is used for the transition rate in ARI, the Hamiltonian needs to be simplified to prepare for the pump stage:

$$\psi_1 \xrightleftharpoons{\text{pumping}} \psi_2.$$

Our derivation of the problem begins with the TDSE:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi, \quad (4)$$

where

$$\hat{H} = \sum_{\alpha}^N \left\{ \frac{1}{2m_{\alpha}} [\vec{p}_{\alpha} - q_{\alpha} \vec{A}(\vec{r}_{\alpha}, t)]^2 + q_{\alpha} \phi(\vec{r}_{\alpha}, t) \right\} + V_0, \quad (5)$$

and the sum runs over both nuclei and electrons,  $\vec{p}_{\alpha} = -i\hbar \vec{\nabla}_{\alpha}$ ,  $V_0$  is the usual interparticle Coulomb potential for the whole system,  $\vec{A}$  is the vector potential,  $\phi$  is the external scalar potential of the electromagnetic laser field,  $c$  is the speed of light, the charge  $q_{\alpha}$  is  $-e$  for electrons and  $+Z_{\alpha}e$  for nuclei, and  $m_{\alpha}$  are the masses of the particles. Though the TDSE is gauge invariant, this Hamiltonian  $\hat{H}(\vec{A}, \phi)$  is not gauge invariant. The  $\phi(\vec{r}_{\alpha}, t)$  term in the Hamiltonian brings in an additional  $\frac{\partial}{\partial t} \chi(\vec{r}_{\alpha}, t)$  term under a gauge transformation.

Here we want to specify that the  $\phi(\vec{r}_\alpha, t)$  is not the total scalar potential for the system, instead it is simply the external scalar potential of the electromagnetic laser field. The total scalar potential is:

$$\phi_{total} = \phi(\vec{r}, t) + \phi_{sys}(\vec{r}, t) \quad (6)$$

where  $\phi_{sys}(\vec{r}, t)$  is the Coulomb potential created by the system itself.

In order to simplify the Hamiltonian, perturbation theory needs to be used if we are using a weak field laser. The Hamiltonian is broken into the unperturbed Hamiltonian (Molecular Hamiltonian)  $\hat{H}_0$ , and the perturbation Hamiltonian  $\hat{H}_{interaction}$ ,

$$\hat{H} = \hat{H}_0 + \hat{H}_{interaction}, \quad (7)$$

where the  $\hat{H}_0$  and  $\hat{H}_{interaction}$  terms are chosen differently based on the associated gauges, as seen in section IV and V, and  $H_0$  always contains the  $V_0$  term.

It is commonly agreed that a gauge can be chosen arbitrarily without further approximation. Yang showed that making the formulation gauge invariant requires the basis-determining Hamiltonian to be the quantum energy operator[7]. The energy operator is  $\hat{H}(\vec{A}, 0)$ , i.e., the Hamiltonian without the scalar potential of the time-dependent field. The wavefunctions associated with the gauge-invariant unperturbed Hamiltonian are gauge independent. The unperturbed Hamiltonian forms for the Coulomb gauge and the Multipolar gauge is derived in section VI to test the gauge invariance property.

The gauge transformed wave function is:

$$\Psi'(\vec{r}; t) = \exp \left[ iq_\alpha \sum_{\alpha} \chi(\vec{r}_\alpha; t) \right] \Psi(\vec{r}; t), \quad (8)$$

where  $\vec{r} = \{\vec{r}_1, \vec{r}_2, \dots\}$  and  $\chi(\vec{r}_\alpha; t)$  is an arbitrary, real, and differentiable function of  $\vec{r}_\alpha$  and  $t$ . Under this transformation the vector potential and the scalar potential satisfy the following[5][6]:

$$\vec{A}'(\vec{r}_\alpha; t) = \vec{A}(\vec{r}_\alpha; t) + \nabla \chi(\vec{r}_\alpha; t) \quad (9)$$

and

$$\phi'(\vec{r}_\alpha; t) = \phi(\vec{r}_\alpha; t) - \frac{\partial}{\partial t} \chi(\vec{r}_\alpha; t). \quad (10)$$

Here we have to specify again that the  $\phi'(\vec{r}_\alpha; t)$  is not the total scalar potential. The transformation relation of the total scalar potential for the system is,

$$\phi'_{total}(\vec{r}_\alpha, t) = \phi_{total}(\vec{r}_\alpha, t) - \frac{\partial}{\partial t} \chi(\vec{r}_\alpha; t) = \phi(\vec{r}_\alpha, t) + \phi_{sys}(\vec{r}_\alpha, t) - \frac{\partial}{\partial t} \chi(\vec{r}_\alpha; t) \quad (11)$$

Then we can choose to let the change to be reflected in the  $\phi'(\vec{r}_\alpha; t)$  term, while  $\phi'_{sys}(\vec{r}_\alpha, t)$  remains unchanged. This is just a choice of breaking two components of the total scalar potential, and it does not break the gauge transformation relation for the scalar potential.

The general gauge transformation does not alter the Time Dependent Schrödinger Equation (TDSE),

$$i\hbar\frac{\partial}{\partial t}\Psi'(\vec{r}; t) = \left\{ \sum_{\alpha}^N \left[ -\frac{\hbar^2}{2m_{\alpha}}\nabla_{\alpha}^2 + i\hbar\frac{q_{\alpha}}{2m}(\vec{A}' \cdot \nabla_{\alpha} + \nabla_{\alpha} \cdot \vec{A}') + \frac{q_{\alpha}^2}{2m}\vec{A}'^2 + q_{\alpha}\phi' \right] + V_0 \right\} \Psi'(\vec{r}; t) \quad (12)$$

or equivalently, the TDSE is gauge invariant. Here we say the  $V_0$  remains unchanged, just because the change of the total scalar potential has been reflected in terms of  $\phi'(\vec{r}_\alpha, t)$ .

#### IV. COULOMB GAUGE IN ARI

The most commonly used gauge is the Coulomb gauge, which is widely used by physicists, especially experimentalists. The Coulomb gauge is said to have the velocity form. As can be deduced in the following procedure, the Hamiltonian will have a velocity form as the perturbation part. The Coulomb gauge is defined as follows:

$$\nabla_{\alpha} \cdot \vec{A}_C(\vec{r}_{\alpha}; t) = 0, \quad (13)$$

where the subscript ‘C’ denotes the Coulomb gauge.

In coherent control of a bimolecular reaction, the source of the E&M field is treated at infinity, so:

$$\phi_C(\vec{r}_{\alpha}; t) = 0. \quad (14)$$

It should be pointed out that the second definition is the radiation gauge for the source free case. This definition is slightly different from the classical Coulomb gauge, while in classical Electrodynamics the Coulomb gauge is defined by Eq.(13). However Eq.(14) is also valid, since one doesn’t need the source information because it is weak. The source is at infinity. The source term then can be neglected without violating the physics.

Now the vector potential satisfies the wave equation:

$$\nabla^2 \vec{A}_C - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{A}_C = 0. \quad (15)$$

Then the time-dependent Schrödinger equation reduces to:

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r};t) = \left\{ \sum_{\alpha}^N \left[ -\frac{\hbar^2}{2m_{\alpha}}\nabla_{\alpha}^2 + i\hbar\frac{q_{\alpha}}{m_{\alpha}}\vec{A}_C \cdot \nabla_{\alpha} + \frac{q_{\alpha}^2}{2m_{\alpha}}\vec{A}_C^2 \right] + V_0 \right\} \Psi(\vec{r};t). \quad (16)$$

The weak field approximation is applied to the Hamiltonian, which assumes the  $\vec{A}^2$  term is negligible and the TDSE above becomes:

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r};t) = \left\{ \sum_{\alpha}^N \left[ -\frac{\hbar^2}{2m_{\alpha}}\nabla_{\alpha}^2 + i\hbar\frac{q_{\alpha}}{m_{\alpha}}\vec{A}_C \cdot \nabla_{\alpha} \right] + V_0 \right\} \Psi(\vec{r};t) \quad (17)$$

Now the Hamiltonian can be broken into two parts:

$$\hat{H} = \hat{H}_0 + \hat{H}_{interaction}, \quad (18)$$

where  $\hat{H}_0$  is defined as :

$$\hat{H}_0 = \sum_{\alpha}^N -\frac{\hbar^2}{2m_{\alpha}}\nabla_{\alpha}^2 + V_0. \quad (19)$$

And the time dependent perturbation term ,  $\hat{H}_{interaction}$ , is defined as:

$$\hat{H}_{interaction} = \sum_{\alpha}^N i\hbar\frac{q_{\alpha}}{m_{\alpha}}\vec{A}_C \cdot \nabla_{\alpha} = \sum_{\alpha}^N -\frac{q_{\alpha}}{m_{\alpha}}\vec{A}_C \cdot \vec{p}_{\alpha} = \sum_{\alpha}^N V_{\alpha}, \quad (20)$$

where classically  $\vec{p} = m\vec{v}$  reveals that the perturbation part ,  $\hat{H}_{interaction}$ , is in the velocity form.

If the vector potential from the system is negligible compared to the external field, according to electrodynamics:

$$\begin{aligned} V_{\alpha} &= -\frac{q_{\alpha}}{m_{\alpha}}\vec{A}_C \cdot \vec{p}_{\alpha} \\ &= -\frac{q_{\alpha}}{m_{\alpha}} \left[ A_0\hat{\epsilon}e^{i(\vec{k}\cdot\vec{r}-\omega t)} - A_0^*\hat{\epsilon}e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \right] \cdot \vec{p}_{\alpha} \\ &\approx \frac{q_{\alpha}}{m_{\alpha}}\frac{E_0}{\omega}(\hat{\epsilon} \cdot \vec{p}_{\alpha}) \sin(\omega t), \end{aligned} \quad (21)$$

where the  $\vec{A}_C$  is simply the external vector potential, the  $E_0$  term is the time independent component of the electric field, and  $\hat{\epsilon}$  is the unit polarization vector of the electric field. The total perturbation term can be written as:

$$\hat{H}_{interaction}(t) = \left( \sum_{\alpha} \frac{q_{\alpha}}{m_{\alpha}}\frac{E_0}{\omega}(\hat{\epsilon} \cdot \vec{p}_{\alpha}) \right) \sin(\omega t). \quad (22)$$

In Eq. (21), a second approximation, called the dipole approximation, is usually applied. The atomic wavefunctions extend to the order of the Bohr radius of the atom, which is approximately  $1\text{\AA}$ , while the wavelength of the pumping or dumping lasers is roughly  $1000\text{\AA}$ . More generally, if  $a$  is a distance which describes the extent of the atomic wave functions, and if  $ka \ll 1$  where  $k$  is the wave number of the laser, one can express  $\exp(i\vec{k} \cdot \vec{r})$  as unity. This approximation is known as the dipole approximation. Because the charged particles are confined in a small region near the atom or molecule, this is also referred as the long-wavelength approximation (LWA), which amounts to neglecting the spatial variation of the radiation field across the atom.

Since we change from an atomic system to an unbound molecular system, Kobe's LWA needs to be verified. Some worried about the LWA in the quantum coherent control problem, for the LWA may not be valid for the three-atom system. For the initial state, the system  $A + BC$  will be kept ultracold, and hence  $A$  may be  $\approx 1000\text{\AA}$  away from the diatom  $BC$ . This seems to violate the LWA, for the lasers that are commonly used have wavelengths of the same order  $\sim 1000\text{\AA}$ . The concern is reasonable: if in a system the electrons move between the two subsystems, one can see that the  $ka \ll 1$  condition is not satisfied. Or equivalently, the LWA will break down.

However, in the coherent control problem, for each of the two subsystems  $A$  and  $BC$ , the LWA is valid. The laser interacts with the electrons that moves adiabatically with respect to the charge center. The electrons will be considered as moving in the subsystems, instead of moving between the subsystems. The electronic wavefunctions are associated with the eigenstates of the atom and a diatom separately. So the distance parameter  $a$  that may be taken into account here is not the system scale but the scale of the subsystems. That is to say the  $a$  term above should be of the order  $1 \sim 10\text{\AA}$  instead of  $1000\text{\AA}$ , so the LWA still applies to our three-atom system.

Using the LWA assumption above, the vector potential and the electric field depend only on time, which is also the same assumption for the Multipolar gauge in section V.

Therefore, the transition rate can be expressed as:

$$W_{kl} = \frac{\pi}{2\hbar} |V_{kl}|^2 [\delta(E_k - E_l - \hbar\omega) + \delta(E_k - E_l + \hbar\omega)], \quad (23)$$

where the matrix element is

$$V_{kl} = \frac{E_0}{m\omega} \left\langle k \left| \hat{\epsilon} \cdot \left( \sum_{\alpha} q_{\alpha} \vec{p}_{\alpha} \right) \right| l \right\rangle, \quad (24)$$

$E_k, E_l$  are energies for the coupled states, and  $\omega$  is the frequency of the incident laser.

This interaction matrix element is said to have a velocity form, since the  $\vec{p}$  term is included. However if we have a local Hamiltonian, then a commutation relation can be applied:

$$[\vec{r}, \hat{H}_0] = \frac{i\hbar\vec{p}}{m}, \quad (25)$$

to transform to a length-like form so that the matrix element can be written as:

$$\begin{aligned} V_{kl} &= \frac{iE_0\omega_{kl}}{\omega} \left\langle k \left| \hat{\epsilon} \cdot \left( \sum_{\alpha} q_{\alpha} \vec{r}_{\alpha} \right) \right| l \right\rangle \\ &= \frac{iE_0\omega_{kl}}{\omega} \langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle \end{aligned} \quad (26)$$

where the  $\hat{\mu}$  term is the electric dipole moment of this system. Here it needs to be specified that this procedure is only valid for a local Hamiltonian. In Eq.(25), in order for the commutation relation to be correct, the molecular Hamiltonian  $H_0$  must be local.

With a local Hamiltonian, the state-to-state transition rate induced by the electric field is:

$$\begin{aligned} W_{kl} &= \frac{\pi}{2\hbar} |E_0|^2 \frac{\omega_{kl}^2}{\omega^2} |\langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle|^2 [\delta(E_k - E_l - \hbar\omega) + \delta(E_k - E_l + \hbar\omega)] \\ &\simeq \frac{\pi}{\hbar^2} |E_0|^2 \frac{\omega_{kl}^2}{\omega^2} |\langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle|^2 [\delta(\omega_{kl} - \omega) + \delta(\omega_{kl} + \omega)] \\ &= \frac{\pi}{\hbar^2} |E_0|^2 |\langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle|^2 [\delta(\omega_{kl} - \omega) + \delta(\omega_{kl} + \omega)] \end{aligned} \quad (27)$$

## V. MULTIPOLAR GAUGE IN ARI

The multipolar gauge is defined as follows [8]:

$$\vec{r} \cdot \vec{A}_M(\vec{r}, t) = 0 \quad (28)$$

with a boundary condition for the transformation function  $\chi_M(\vec{r}, t)$  at the origin:

$$\phi(0, t) - \frac{\partial}{\partial t} \chi_M(0, t) = 0, \quad (29)$$

where the subscript ‘M’ denotes the Multipolar gauge.

Under multipolar gauge the vector potential and the scalar potential are easily expressed in terms of  $\vec{E}$  and  $\vec{B}$  field:

$$\vec{A}_M(\vec{r}, t) = -\vec{r} \times \int_0^1 u \vec{B}(u\vec{r}, t) du \quad (30)$$

$$\phi_M = -\vec{r} \cdot \int_0^1 \vec{E}(u\vec{r}, t) du, \quad (31)$$

in which we know that both  $\vec{E}$  and  $\vec{B}$  are gauge invariant.

A multipole expansion of the potentials in Eq.(30), Eq. (31) can be made by expanding the fields about the origin. Under the LWA, only the first few terms of the expansion need to be included:

$$\vec{A}_M(\vec{r}, t) = -\frac{1}{2}\vec{r} \times \vec{B}(0, t) + \dots \quad (32)$$

$$\phi_M = -\vec{r} \cdot \vec{E}(0, t) - \frac{1}{2}r_i r_j \partial'_j E_i(\vec{r}', t)|_{\vec{r}'=0} + \dots \quad (33)$$

If we neglect the electric quadrupole and magnetic dipole terms, one obtain the electric dipole approximation (EDA) for  $\vec{A}_M, \phi_M$  as:

$$\vec{A}_M(\vec{r}, t) \approx 0 \quad (34)$$

$$\phi_M \approx -\vec{r} \cdot \vec{E}(0, t). \quad (35)$$

Combining the LWA with the EDA the Hamiltonian becomes

$$\hat{H}^E = \sum_{\alpha} \frac{1}{2m_{\alpha}} \vec{p}_{\alpha}^2 + V_0 - \hat{\mu} \cdot \vec{E}(t) = H_0 - \hat{\mu} \cdot \vec{E}(t), \quad (36)$$

where

$$\hat{\mu} = \sum_{\alpha} q_{\alpha} \vec{r}_{\alpha} \quad (37)$$

is the dipole moment operator. The time-independent part of the Hamiltonian,  $\hat{H}_0$ , is

$$\hat{H}_0 = \sum_{\alpha} \frac{1}{2m_{\alpha}} \vec{p}_{\alpha}^2 + V_0. \quad (38)$$

Since the perturbation part in the Hamiltonian under the Multipolar gauge transformation has a  $\vec{r}$  term, it is said that the Multipolar gauge has a length form.

Some call the Multipolar gauge treatment with the electric dipole approximation as the Electric field gauge[9], and this Electric field gauge is still controversial. The main problem is with the Electric field gauge is that  $\vec{A}_M \approx 0$ . In a gauge transformation, the function

$\chi(\vec{r}_\alpha, t)$  is arbitrary. However, it should not violate the physics. It can be seen that, from electrodynamics,

$$\vec{B} = \nabla \times \vec{A},$$

which means  $\vec{B} \approx 0$  for the Electric field gauge, which is not true.

The Electric field gauge is not a real gauge. However, the gauge we applied in the first place is the Multipolar gauge. The Multipolar gauge, which is also called the nonrelativistic Poincaré gauge or four dimensional Fock-Schwinger gauge, is a real gauge, and does not violate Maxwell's equations. Then approximations are used in ARI, and we have shown that the LWA and weak field approximation have to be used in the Coulomb gauge. We will use the LWA and the electric dipole approximation in the Multipolar gauge. It means that with this treatment one obtain the correct gauge form for the Hamiltonian, without violating the basic physics to first order, then the treatment is reasonable and comparable to other real gauge treatments.

Also as in Kobe's paper[9], the Multipolar gauge with EDA does not violate the Maxwell equations. As Kobe pointed out:

1. The EDA does not describe the electromagnetic field itself, but only approximates the effect of the field on the atom in the long wavelength limit.
2. The EDA requires only the electric field at the origin  $\vec{E}(0, t)$ , which can be obtained from a scalar potential alone even though  $\vec{E}$  is transverse.
3. In the EDA the magnetic multipoles are neglected. This approximation is equivalent to neglecting the spatial variation of the vector potential  $\vec{A}(0, t)$  in the Coulomb gauge. The vector  $\vec{A}(0, t)$  can then be eliminated by a gauge transformation.

The two approximations in the Multipolar gauge treatment are:

- Electric dipole approximation.
- The long-wavelength approximation (LWA).

The first approximation is reasonable when the magnetic dipole effect and the electric quadrupole effect are much smaller than the electric dipole effect in the particle-field interaction. What is more, the approximation here is to first order in electric potential  $\phi$ . The Coulomb gauge approximation is to first order in the vector potential  $\vec{A}$ , and the  $\vec{A}^2$  term is

negligible, under the weak field assumption. At least from the approximation's perspective, the Multipolar gauge treatment and Coulomb gauge treatment are both approximated to the first order. Though they have different forms for the interaction, both of the gauges approximate to the first order of the transition rates.

The second approximation, the long-wavelength approximation (LWA), has been stated above when LWA was applied to Coulomb gauge in Section IV. Since it is the same system, the LWA is still valid in Multipolar gauge.

Therefore the transition rate matrix element can be written as:

$$\begin{aligned}
V_{kl} &= \langle k | \hat{H}_{interaction} | l \rangle \\
&= - \sum_{\alpha} \langle k | q_{\alpha} E_0 \hat{\epsilon} \cdot \vec{r}_{\alpha} | l \rangle \\
&= -E_0 \langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle,
\end{aligned} \tag{39}$$

so that the Multipolar gauge transition rate is:

$$\begin{aligned}
W_{kl} &= \frac{\pi}{2\hbar} |E_0|^2 \langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle^2 [\delta(E_k - E_l - \hbar\omega) + \delta(E_k - E_l + \hbar\omega)] \\
&\simeq \frac{\pi}{\hbar^2} |E_0|^2 \langle k | \hat{\epsilon} \cdot \hat{\mu} | l \rangle^2 [\delta(\omega_{kl} - \omega) + \delta(\omega_{kl} + \omega)].
\end{aligned} \tag{40}$$

Compared with Eq.(27), for the ARI in a three-atom system under local and resonance conditions, the same transition rate with Coulomb gauge and the Multipolar gauge could be obtained. In other words, the two forms can be transformed into each other only if the molecular Hamiltonian is local.

## VI. CHOOSING CRITERIA

When perturbation theory is applied, the question arises as to whether these two Hamiltonians, which depend on different gauge transformations, will give different answers and which will be better.

In 1978, Donald H. Kobe proved that for a non-resonant, two-photon absorption processes, the results for the length form and the velocity form are not the same. It can be seen in Eq.(15) from Kobe's paper[5]:

$$M_p = M_r + (1 + \hat{P}_{12}) \frac{\Delta}{\omega_2} \sum_n \frac{\langle 2s | e\vec{E}_2 \cdot \vec{r} | n \rangle \langle n | e\vec{E}_1 \cdot \vec{r} | 1s \rangle}{E_n - E_{1s} - \omega_1} + \frac{\Delta}{\omega_1 \omega_2} \langle 2s | (e\vec{E}_1 \cdot \vec{r})(e\vec{E}_2 \cdot \vec{r}) | 1s \rangle$$

that, the matrix elements for the interaction term are not equal to each other if  $\Delta$  is non zero. In this equation  $M_p$  is the Coulomb gauge interaction matrix element,  $M_r$  is the Multipolar gauge interaction matrix element, and the frequency difference variable  $\Delta$  is defined as:

$$E_{2s} = E_{1s} + \omega_1 + \omega_2 + \Delta.$$

Other variables in this equation, are defined in detail in Kobe's paper[5].

Also in 1979 Kobe[6] pointed out, that "as the eigenstates of the molecular Hamiltonian are to be used as the basis states, the electric dipole interaction in the length form is the proper perturbation".

Let's take a look into gauge invariance for the Multipolar gauge. Eq.(38) shows the expression for the unperturbed part  $\hat{H}_0$ , which is the molecular Hamiltonian in absence of the electromagnetic field. Then one can have:

$$\hat{H}_0 \Phi_n = E_n \Phi_n, \quad (41)$$

and the wavefunction can be expanded into:

$$\Psi = \sum_n c_n \Phi_n. \quad (42)$$

In order to look into the properties of this molecular Hamiltonian, it can be seen that for Eq.(38):

$$\hat{H}_0 = \sum_{\alpha}^N \frac{1}{2m_{\alpha}} [\vec{p}_{\alpha} - q_{\alpha} \vec{A}_M(r, t)]^2 + V_0 \approx \sum_{\alpha}^N \frac{1}{2m_{\alpha}} \vec{p}_{\alpha}^2 + V_0, \quad (43)$$

the molecular Hamiltonian or the unperturbed Hamiltonian is an energy operator which is gauge invariant. Some argue that the form of Eq. (38) does not exclusively depend on the field  $\vec{A}$ . However,  $\vec{A}$  is indeed included in this unperturbed Hamiltonian, and the value of it is zero. This Hamiltonian is then gauge invariant, so that the coefficients are not gauge dependent, which could be transformed to other coefficients from any other gauge-based calculations. The basis wavefunction  $\Phi_n$  are not time dependent either, because the molecular Hamiltonian  $H_0$  is not time dependent.

In order to verify the gauge invariant property of the length form, we have to look into the perturbation Hamiltonian, which is expressed as:

$$\hat{H}_{interaction} = -\hat{\mu} \cdot \vec{E}(t). \quad (44)$$

And if we do a vertical excitation  $\vec{E}(t) = \vec{E}(t_0)$ , and  $t_0$  is the initial time. The length form (Multipolar gauge) of interaction does not have a gauge dependent part.  $H_{interaction}$  is manifestly gauge invariant because it explicitly involves the electric field. It can be seen from section III that, the electric field  $\vec{E}$  is gauge invariant.

When the Coulomb gauge transformation is applied without approximations, the TDSE is still gauge invariant. But in this case we need to break the Hamiltonian into an unperturbed part  $H_0$  and a perturbed part  $\hat{H}_{interaction}$  in Eq.(20). Therefore the restriction of gauge invariance will be problematic for the Coulomb gauge transformation[5].

The expansion of Hamiltonian in the Coulomb gauge breaks the manifest gauge invariance. The velocity form of the interaction can be expressed as

$$\hat{H}_{interaction} = - \sum_{\alpha} \frac{q_{\alpha}}{mc} \vec{A}_c \cdot \vec{p}_{\alpha}. \quad (45)$$

This expression is the perturbation part, while the expansion coefficients of the wave function  $\Psi$  in terms of the molecular states  $\Phi_n$  are gauge dependent, and are therefore not proper to obtain the probability amplitudes. Let us look into the unperturbed Hamiltonian:

$$\hat{H}_0 = \sum_{\alpha} \frac{1}{2m_{\alpha}} \vec{p}_{\alpha}^2 + V \neq \sum_{\alpha} \frac{1}{2m_{\alpha}} [\vec{p}_{\alpha} - q_{\alpha} \vec{A}_C(r, t)]^2 + V_0. \quad (46)$$

Now it does not depend on the vector field  $\vec{A}$ , which means the molecular Hamiltonian obtained from the velocity form is not a gauge invariant Hamiltonian.

This form of the unperturbed Hamiltonian looks exactly like the Multipolar gauge case, which might lead to confusion. However, the problem actually can be viewed in terms of the perturbation Hamiltonian. Since the interaction part of the Hamiltonian involves the vector potential  $\vec{A}$ , the treatment is not gauge independent or gauge invariant. The vector potential, “velocity” interaction, can be added with any arbitrary term  $\nabla\chi$ . The Hamiltonian will be changed because of the term  $\nabla\chi$  without changing any physical situation, if  $\chi$  satisfies Laplace’s equation.

A summary of this section can be seen in table I.

	Coulomb gauge	Multipolar gauge
Definition	$\nabla \cdot \vec{A}_C = 0$ $\phi_C = 0$	$\vec{r} \cdot \vec{A}_M(\vec{r}, t) = 0$ $\phi(0, t) - \frac{\partial}{\partial t} \chi_M(0, t) = 0$
Approximation Used	WFA LWA	EDA LWA
molecular Hamiltonian	$\sum_{\alpha}^N -\frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 + V_0$	$\sum_{\alpha}^N \frac{1}{2m_{\alpha}} [\vec{p}_{\alpha} - q_{\alpha} \vec{A}_M(\vec{r}, t)]^2 + V_0$
$H_{interaction}$	$-\sum_{\alpha} \frac{q_{\alpha}}{mc} \vec{A}_C \cdot \vec{p}_{\alpha}$	$-\vec{\mu} \cdot \vec{E}$
Matrix Element	$\frac{E_0}{m\omega} \langle k   \hat{\epsilon} \cdot \sum_{\alpha} q_{\alpha} \vec{p}_{\alpha}   l \rangle$	$-E_0 \langle k   \hat{\epsilon} \cdot \vec{\mu}   l \rangle$
Interaction Form	Velocity form	Length Form
With Local Hamiltonian	Can be transformed to other forms using $[\vec{r}, \vec{p}] = i\hbar$	Can be transformed to other forms using $[\vec{r}, \vec{p}] = i\hbar$
With Nonlocal Hamiltonian	Can not be transformed to other forms	Can not be transformed to other forms

Table I: The main properties of the Coulomb gauge and the Multipolar gauge

## VII. CONCLUSION

From this paper, I show that:

1. In the quantum coherent control problem, the Coulomb gauge and Multipolar gauge use reasonable approximations. Though the Multipolar gauge with EDA is controversial, it is the proper gauge to use for bimolecular quantum control.
2. For ARI of quantum coherent control, if the Hamiltonian is local the velocity form and length form can be transformed to each other; if the Hamiltonian is nonlocal, the two forms can not be transformed into each other.
3. On the basis of gauge invariance, the length form is considered to be more fundamental and should be used in any calculations.

If the Hamiltonian is local, the length form can be transformed into velocity form. In atomic physics, the full many-body Hamiltonian equals the sum of kinetic operators for all particles in the system and two-particle Coulomb potential energy operators for all pairs of particles. These potential energies are, of course, local. However, exact wavefunctions are not

usually computed due to limited computation powers, and approximations have to be used to obtain the wavefunctions. Different models will give different approximate wavefunctions, depending on which gauge is used. If a nonlocal Hamiltonian is applied in a calculation, it might lead to two different results with the Coulomb gauge and the Multipolar gauge. The Hartree-Fock method and other methods commonly used in theoretical calculations, use nonlocal Hamiltonian models.

When deciding which form to choose, the key point is whether the molecular Hamiltonian or unperturbed Hamiltonian under a transformation is gauge invariant or not. One needs to be careful about whether the Hamiltonian is gauge invariant, so that the calculation is based on the gauge independent probability density function. From Section VI, it shows that the Multipolar gauge molecular Hamiltonian is gauge invariant, and the associated wavefunctions are gauge independently calculated. In the Coulomb gauge the molecular Hamiltonian is gauge variant, and the associated wavefunctions are gauge dependent.

In conclusion, the Multipolar gauge gives the same transition rate as the Coulomb gauge in ARI of coherent control with a local Hamiltonian. When a nonlocal exact Hamiltonian or nonlocal model Hamiltonian is used, the two forms give different results. On the basis of gauge invariance, the Multipolar gauge in coherent control should be favored to simplify the Hamiltonian, since it more accurately represents nature. Here we use a common idea that nature is gauge invariant.

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