Gauge-invariant time-dependent perturbation theory. I. Non-degenerate case



1982 J. Phys. A: Math. Gen. 15 1201

(http://iopscience.iop.org/0305-4470/15/4/023)

J. Phys. A: Math. Gen. **15** (1982) 1201–1216. Printed in Great Britain

# Gauge-invariant time-dependent perturbation theory: I. Non-degenerate case

Kuo-Ho Yang†

Department of Physics and Astronomy, University of Maryland, College Park, Md 20742, USA and
Theoretical Chemistry Institute, University of Wisconsin, Madison, Wi 53706, USA

Received 15 May 1981, in final form 3 November 1981

**Abstract.** A manifestly gauge-invariant time-dependent perturbation theory is developed for a non-degenerate quantum mechanical system interacting with an arbitrary classical electromagnetic radiation field. The first- and second-order net transition rates are derived and compared with their conventional counterparts. It is found that the conventional and the gauge-invariant perturbative rates of transition agree completely.

## 1. Introduction

In a previous paper (Yang 1982), we have shown that the conventional interpretation of the quantum mechanical probability amplitudes and probabilities is *gauge dependent* and, when applied to the relativistic (Dirac) and the non-relativistic quantum mechanics, can *not* be consistent with the Foldy–Wouthuysen transformations (Foldy and Wouthuysen 1950). We have also shown that these two difficulties are *not* present in a gauge-invariant formulation proposed previously (Yang 1976, Kobe and Smirl 1978, Leubner and Zoller 1980) that incorporates Poynting's theorem and the conservation law of energy (Jackson 1975) into the definition of probability amplitudes.

The above findings are true for the *exact* probability amplitudes and probabilities. They thus raise an important question as to how some *approximate* solutions from these two formulations will compare with each other. In this series of papers, we shall address ourselves to the *perturbative* results that are the most familiar and commonly used approximate solutions to the Schrödinger equation.

In this paper we shall concentrate on a non-degenerate system and develop a manifestly gauge-invariant time-dependent perturbation theory for such a system.‡ The formulation to be developed here will serve as the basis for our later treatment of a more complicated system. Throughout this paper, we shall assume that the 'unperturbed' Hamiltonian has a *non*-degenerate spectrum. In addition, we also assume that the *magnetic* field involved is not strong enough to cause a breakdown of the Rayleigh–Schrödinger time-independent perturbation theory (RSTIPT) (e.g. Messiah 1966) in solving for the eigenvalues and eigenfunctions of the gauge-invariant energy operator $H_B$.

† Present address: Theoretical Chemistry Institute, University of Wisconsin, Madison, Wi 53706, USA.
‡ A brief account of this paper can be found in Yang (1981).

0305-4470/82/041201+16$02.00  

This paper contains six sections. In § 2 we shall briefly review the gauge-invariant formulation and the physical concepts involved. In § 3, we first solve for the eigenvalues and eigenfunctions of the energy operator $H_B$ by the RSTIPT and then apply these results to formulate a time-dependent perturbation theory (TDPT). Here, we shall also describe a procedure for evaluating the transition matrix elements and prove the manifest gauge invariance of these transition matrix elements through the second order.

In § 4 we use a single-frequency external field to obtain the first-order and second-order perturbative rates of transitions. Here, we also make the extra effort to use this simple field to demonstrate that, despite our choice of the arbitrary potentials, the transition matrix elements depend explicitly only on the fields. In § 5, we briefly compare our first- and second-order net transition rates with their conventional counterparts and find complete agreement between these rates of transitions. Finally, a brief discussion is presented in § 6.

## 2. The gauge-invariant formulation

In this section we shall briefly review the gauge-invariant formulation of a quantised particle interacting with a classical external electromagnetic field. For a more complete description of the theory, see Yang (1976) and Kobe and Smirl (1978). A *very* detailed discussion of the concept of gauge invariance in both classical and quantum mechanics can be found in Cohen-Tannoudji *et al* (1977). Some simple applications of this formulation to gauge-related problems have been made by Yang (1976), Kobe and Smirl (1978) and, more recently, Leubner and Zoller (1980).

Let us consider a non-relativistic, spinless particle with mass $m$ and charge $e$ interacting with a conservative, electrostatic field $\boldsymbol{E}_0(\boldsymbol{r}) = -\nabla V_0(\boldsymbol{r})$ and a time-varying electromagnetic radiation field $\boldsymbol{E}(\boldsymbol{r}, t)$ and $\boldsymbol{B}(\boldsymbol{r}, t)$. If we use the potentials $\boldsymbol{A}(\boldsymbol{r}, t)$ and $\Phi(\boldsymbol{r}, t)$ in an arbitrary gauge to represent $\boldsymbol{E}(\boldsymbol{r}, t)$ and $\boldsymbol{B}(\boldsymbol{r}, t)$, then

$$\boldsymbol{E} = -\nabla\Phi - (1/c)\,\partial\boldsymbol{A}/\partial t, \qquad \boldsymbol{B} = \nabla\times\boldsymbol{A}. \tag{2.1}$$

In this gauge, the Hamiltonian and the Schrödinger equation are

$$H = (\boldsymbol{p} - e\boldsymbol{A}/c)^2/2m + eV_0 + e\Phi, \tag{2.2}$$

$$\mathrm{i}\hbar\dot{\Psi}(\boldsymbol{r}, t) = H\Psi(\boldsymbol{r}, t), \tag{2.3}$$

where $\dot{\Psi} = \partial\Psi/\partial t$.

The central idea of the gauge-invariant formulation is to construct, for the Hamiltonian in (2.2), the energy operator $H_B$ representing the particle's energy that conserves with the radiation field energy and its flux. Then we use the eigenfunctions of $H_B$ and the wavefunction to define the probability amplitudes (Yang 1976, 1982, Kobe and Smirl 1978, Leubner and Zoller 1980). According to Poynting's theorem and the conservation law of energy (Jackson 1975, equations (6.110) and (6.111), Yang 1982, § 6) and the correspondence principle (Bohr 1928), the operator $H_B$ is determined, if we *neglect* the self-interaction, by

$$(\mathrm{d}H_B/\mathrm{d}t)_H = \tfrac{1}{2}(\boldsymbol{J}\cdot\boldsymbol{E} + \boldsymbol{E}\cdot\boldsymbol{J}) \equiv P(t), \tag{2.4}$$

where

$$(\mathrm{d}H_B/\mathrm{d}t)_H = \partial H_B/\partial t + [H_B, H]/\mathrm{i}\hbar \tag{2.5}$$

and $P(t)$ will be referred to as the power operator throughout this paper. The symbol $\boldsymbol{J}$ in (2.4) is the current operator associated with the Hamiltonian in (2.2) and hence is $e\boldsymbol{v}$ where $\boldsymbol{v} = [\boldsymbol{r}, H]/\mathrm{i}\hbar = (\boldsymbol{p} - e\boldsymbol{A}/c)/m$. If we use $H$ in (2.2) and this expression of $\boldsymbol{J}$ in (2.4) and (2.5), we find

$$H_B(t) = (\boldsymbol{p} - e\boldsymbol{A}/c)^2/2m + eV_0 = \tfrac{1}{2}m\boldsymbol{v}^2 + eV_0, \tag{2.6}$$

which is just the sum of the *Newtonian* kinetic energy and the potential energy.

Let us use $\{E_j(t)\}$ and $\{\Psi_j(\boldsymbol{r}, t)\}$ to denote the eigenvalues and the orthonormal and complete (assumed) set of eigenfunctions of $H_B(t)$. That is

$$H_B(t)\Psi_j(\boldsymbol{r}, t) = E_j(t)\Psi_j(\boldsymbol{r}, t), \qquad \langle\Psi_j|\Psi_k\rangle = \delta_{jk}. \tag{2.7}$$

Note, the time dependence in $E_j(t)$ and $\Psi_j(\boldsymbol{r}, t)$ is solely determined by the time dependence in $\boldsymbol{A}(\boldsymbol{r}, t)$. However, the $\{E_j\}$ reduce to the time-independent spectrum of $H_0 = \boldsymbol{p}^2/2m + eV_0$ if $\nabla \times \boldsymbol{A} = 0$ since now $\boldsymbol{A} = \nabla\chi$ and $H_B = RH_0R^\dagger$ where $R = \exp(\mathrm{i}e\chi/c\hbar)$.

We then expand the wavefunction $\Psi(\boldsymbol{r}, t)$ in the basis of $\{\Psi_j(\boldsymbol{r}, t)\}$ with the expansion coefficients $\{a_j(t)\}$,

$$\Psi(\boldsymbol{r}, t) = \sum_j a_j(t)\Psi_j(\boldsymbol{r}, t), \qquad a_j(t) = \langle\Psi_j(t)|\Psi(t)\rangle, \tag{2.8}$$

and interpret $\{a_j(t)\}$ as probability amplitudes. These probability amplitudes satisfy the differential equation

$$\mathrm{i}\hbar\dot{a}_j = E_j a_j + \sum_k a_k\langle\Psi_j|(e\Phi - \mathrm{i}\hbar\,\partial/\partial t)|\Psi_k\rangle, \tag{2.9}$$

where $\dot{a}_j = \mathrm{d}a_j(t)/\mathrm{d}t$. It can be shown that $a_j$, $E_j$ and $\langle\Psi_j|(e\Phi - \mathrm{i}\hbar\,\partial/\partial t)|\Psi_k\rangle$ are gauge invariant for all $j$ and $k$ and at all times (Yang 1976, Kobe and Smirl 1978). Hence, equation (2.9) is *manifestly* gauge invariant.

The energy spectrum $\{E_j(t)\}$ will in general be time dependent if there is a time-dependent *magnetic* field. For a *periodic* external field with period $\tau$, we define the *mean* energy spectrum $\{\varepsilon_j\}$ by

$$\varepsilon_j = (1/\tau)\int_0^\tau \mathrm{d}t\, E_j(t). \tag{2.10}$$

The physical meaning of the transition matrix elements in equation (2.9) has been investigated in detail before (Yang 1976, Kobe and Smirl 1978). If we differentiate both sides of the eigenvalue equation (2.7) with respect to time, then

$$(H_B - E_k)(\partial\Psi_k/\partial t) = (\dot{E}_k - \partial H_B/\partial t)\Psi_k, \tag{2.11}$$

where $\dot{E}_k$ is the time derivative of $E_k$. From this and the commutator relation

$$[H_B, e\Phi] = -\tfrac{1}{2}\mathrm{i}\hbar\{\boldsymbol{J}\cdot(\nabla\Phi) + (\nabla\Phi)\cdot\boldsymbol{J}\} \tag{2.12}$$

where $\boldsymbol{J} = e\boldsymbol{v}$, we get

$$(E_j - E_k)\langle\Psi_j|(e\Phi - \mathrm{i}\hbar\,\partial/\partial t)|\Psi_k\rangle = -\mathrm{i}\hbar(E_k\delta_{jk} - \langle\Psi_j|P|\Psi_k\rangle), \tag{2.13}$$

where $P$ has been defined in (2.4).

From (2.13), we obtain

$$\dot{E}_j(t) = \langle\Psi_j|P(t)|\Psi_j\rangle, \tag{2.14}$$

and for $E_j \neq E_k$,

$$\langle \Psi_j | (e\Phi - i\hbar\, \partial/\partial t) | \Psi_k \rangle = i\hbar \langle \Psi_j | P | \Psi_k \rangle / (E_j - E_k). \tag{2.15}$$

The expression in (2.15) indicates that the power operator $P$ governs the transitions between states of different energies. This is consistent with the physical meaning of Poynting's theorem in the classical electromagnetic theory since it is the power density that determines the energy exchange between the radiation field and the charged particle (Jackson 1975, equations (6.110) and (6.111); Yang 1982, § 6).

In the remaining portion of this paper, we will develop a time-dependent perturbation theory for equation (2.9). Because the transition matrix elements in this equation involve the eigenfunctions of $H_B$ instead of the eigenfunctions of the unperturbed Hamiltonian as in the conventional TDPT, we must first solve for $E_j$ and $\Psi_j$ perturbatively. For this purpose, we will need the usual RSTIPT, in which the time is treated as a parameter. In the RSTIPT, a degenerate system is treated differently from a non-degenerate one (e.g. Messiah 1966). In this paper, we shall concentrate on the non-degenerate case. Once the perturbative solutions of $E_j$ and $\Psi_j$ are obtained, we obtain our TDPT simply by substituting these perturbative solutions for $E_j$ and $\Psi_j$ into (2.9), as shown in the next section.

## 3. Gauge-invariant time-dependent perturbation theory

Our purpose in this section is to develop a perturbative treatment to solve (2.9). The TDPT to be formulated here is the Rayleigh–Schrödinger type of perturbation theory, whose solutions can be readily compared with the results from the conventional TDPT. The arrangement of this section is as follows. First, we use the Rayleigh–Schrödinger time-independent perturbation theory to solve for the eigenvalues and eigenfunctions of (2.7). We then use these solutions in (2.9) to obtain a TDPT. After this is done, a procedure for obtaining the gauge-invariant transition matrix elements will be described and their gauge invariance will be shown through the second order.

### *3.1. The Rayleigh–Schrödinger procedure*

According to the RSTIPT (e.g. Messiah 1966), we decompose $H_B$ in (2.6) as

$$H_B = H_0 + V_1 + V_2; \qquad V_1 = -e(\boldsymbol{p}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{p})/2mc, \qquad V_2 = (e\boldsymbol{A})^2/2mc^2, \tag{3.1}$$

where $H_0 = \boldsymbol{p}^2/2m + eV_0$ is the usual 'unperturbed' Hamiltonian. If we substitute (3.1) and the expansions

$$E_j = \sum_n E_j^{(n)} \quad \text{and} \quad \Psi_j = \sum_n \Psi_j^{(n)} \tag{3.2}$$

into (2.7), then, if we use $\varphi_j(\boldsymbol{r})$ for $\Psi_j^{(0)}$ and $\hbar\omega_j$ for $E_j^{(0)}$,

$$(H_0 - \hbar\omega_j)\varphi_j(\boldsymbol{r}) = 0, \tag{3.3}$$

$$(H_0 - \hbar\omega_j)\Psi_j^{(1)} + (V_1 - E_j^{(1)})\varphi_j = 0, \tag{3.4}$$

$$(H_0 - \hbar\omega_j)\Psi_j^{(2)} + (V_1 - E_j^{(1)})\Psi_j^{(1)} + (V_2 - E_j^{(2)})\varphi_j = 0, \tag{3.5}$$

and so on. The normalisation required here is

$$\langle\Psi_j|\Psi_k\rangle=\langle\varphi_j|\varphi_k\rangle=\delta_{jk}. \tag{3.6}$$

In particular (Langhoff *et al* 1972),

$$\sum_{m=0}^{n}\langle\Psi_j^{(m)}|\Psi_j^{(n-m)}\rangle=0 \qquad \text{for all } n\geqslant 1. \tag{3.7}$$

As discussed in the Appendix, consideration of gauge transformations requires that $\langle\varphi_j|\Psi_j^{(1)}\rangle$ should *not* be chosen to vanish. Our particular choices of the values of $\langle\varphi_j|\Psi_j^{(n)}\rangle$ for $n=1$, and 2, are discussed in the Appendix.

From equations (3.4), (3.5) and so on, it can be shown (e.g. Yang 1977) that the eigenvalue corrections $E_j^{(n)}$ are (i) independent of the values of $\{\langle\varphi_j|\Psi_j^{(n)}\rangle\}$, and (ii) gauge invariant for all $j$ and to all orders. The proofs of these two properties of the RSTIPT are straightforward, as the reader can verify for himself.

### *3.2. Time-dependent perturbation theory*

If we substitute the expansions in (3.2) and

$$a_j(t)=\sum_n b_j^{(n)}(t)\exp(-\mathrm{i}\omega_j t) \tag{3.8}$$

into equation (2.9), and then regroup terms of the same order, we get the basic differential equations for the TDPT:

$$\mathrm{i}\hbar\dot{b}_j^{(0)}=0, \tag{3.9}$$

$$\mathrm{i}\hbar\dot{b}_j^{(1)}=\sum_k b_k^{(0)}M_{jk}^{(1)}\exp(\mathrm{i}\omega_{jk}t), \tag{3.10}$$

$$\mathrm{i}\hbar\dot{b}_j^{(2)}=\sum_k\{b_k^{(1)}M_{jk}^{(1)}+b_k^{(0)}M_{jk}^{(2)}\}\exp(\mathrm{i}\omega_{jk}t), \tag{3.11}$$

and so on. Here, $\dot{b}_j^{(n)}=\mathrm{d}b_j^{(n)}/\mathrm{d}t$, $\omega_{jk}=\omega_j-\omega_k$, and

$$M_{jk}^{(n)}=E_j^{(n)}\delta_{jk}+\sum_{m=1}^{n}\langle\Psi_j^{(n-m)}|\xi_k^{(m)}\rangle, \qquad n\geqslant 1, \tag{3.12}$$

where, denoting $\partial\Psi_k^{(m)}/\partial t$ by $\dot{\Psi}_k^{(m)}$,

$$\xi_k^{(m)}=e\Phi\Psi_k^{(m-1)}-\mathrm{i}\hbar\dot{\Psi}_k^{(m)}, \qquad m\geqslant 1. \tag{3.13}$$

Because equations (3.9)–(3.11) are identical in form to the differential equations in the conventional TDPT (e.g. Merzbacher 1961), the usual way of computing the rates of transition can be immediately applied once the transition matrix elements are known. Because these transition matrix elements are defined in a complicated fashion as shown in (3.12) and (3.13), we will first establish a procedure to evaluate them in the next subsection. Finally, we note that the wavefunction $\Psi(r,t)$, when expressed in terms of $\{b_j^{(n)}\}$ and $\{\Psi_j^{(n)}\}$, is

$$\Psi(r,t)=\sum_j\sum_{n=0}^{\infty}\sum_{m=0}^{n}b_j^{(n-m)}\Psi_j^{(m)}\exp(-\mathrm{i}\omega_j t). \tag{3.14}$$

*3.3. Evaluation of transition matrix elements*

For the purpose of the time-dependent perturbation theory, let us first decompose the power operator $P$ in (2.4) as $P = P^{(1)} + P^{(2)}$, where

$$P^{(1)} = e(\boldsymbol{p}\cdot\boldsymbol{E} + \boldsymbol{E}\cdot\boldsymbol{p})/2m = \partial V_1/\partial t + [H_0, e\Phi]/i\hbar, \tag{3.15}$$

$$P^{(2)} = -e^2\boldsymbol{E}\cdot\boldsymbol{A}/mc = \partial V_2/\partial t + [V_1, e\Phi]/i\hbar, \tag{3.16}$$

where the operators $H_0$, $V_1$ and $V_2$ are defined in (3.1), and $\Phi$ is the scalar potential in (2.1).

To derive the expressions for $M_{jk}^{(n)}$, we first derive the equations that $\{\xi_k^{(n)}\}$ satisfy. Multiplying $e\Phi$ from the left to (3.3) and differentiating (3.4) with respect to time, we have (upon changing $j$ into $k$)

$$(H_0 - \hbar\omega_k)(e\Phi\varphi_k) = [H_0, e\Phi]\varphi_k,$$

$$(H_0 - \hbar\omega_k)\dot{\Psi}_k^{(1)} = -(\partial V_1/\partial t - \dot{E}_k^{(1)})\varphi_k.$$

If we use $P^{(1)}$ in (3.15), then

$$(H_0 - \hbar\omega_k)\xi_k^{(1)} = i\hbar(P^{(1)} - \dot{E}_k^{(1)})\varphi_k. \tag{3.17}$$

Similarly, from (3.4), (3.5), (3.15) and (3.16), we have

$$(H_0 - \hbar\omega_k)\xi_k^{(2)} + (V_1 - E_k^{(1)})\xi_k^{(1)} = i\hbar(P^{(1)} - \dot{E}_k^{(1)})\Psi_k^{(1)} + i\hbar(P^{(2)} - \dot{E}_k^{(2)})\varphi_k. \tag{3.18}$$

From (3.17) we get

$$\dot{E}_k^{(1)} = \langle\varphi_k|P^{(1)}|\varphi_k\rangle, \tag{3.19}$$

$$M_{jk}^{(1)} = (i/\omega_{jk})\langle\varphi_j|P^{(1)}|\varphi_k\rangle, \qquad j \neq k. \tag{3.20}$$

The diagonal matrix elements $M_{jj}^{(1)}$ can be obtained from (A13). Thus,

$$M_{jj}^{(1)} = E_j^{(1)} + \eta_j^{(1)}, \qquad \eta_j^{(1)} = \langle\varphi_j|F[-e\boldsymbol{E}]|\varphi_j\rangle. \tag{3.21}$$

To derive the second-order transition matrix elements $M_{jk}^{(2)}$ from (3.18), we first take the projection of this equation onto $\varphi_j$. If we also use (3.4) and (3.17), then it can be shown that

$$\langle\varphi_j|(V_1 - E_k^{(1)})|\xi_k^{(1)}\rangle = \hbar\omega_{jk}\langle\Psi_j^{(1)}|\xi_k^{(1)}\rangle + (E_j^{(1)} - E_k^{(1)})\langle\varphi_j|\xi_k^{(1)}\rangle - i\hbar\langle\Psi_j^{(1)}|(P^{(1)} - \dot{E}_k^{(1)})|\varphi_k\rangle. \tag{3.22}$$

From (3.18) and (3.22), we obtain the following two results. If we set $j = k$ and use $\langle\varphi_k|\Psi_k^{(1)}\rangle + \langle\Psi_k^{(1)}|\varphi_k\rangle = 0$, then

$$\dot{E}_k^{(2)} = \langle\varphi_k|P^{(1)}|\Psi_k^{(1)}\rangle + \langle\Psi_k^{(1)}|P^{(1)}|\varphi_k\rangle + \langle\varphi_k|P^{(2)}|\varphi_k\rangle. \tag{3.23}$$

For $j \neq k$, we use $\langle\varphi_j|\Psi_k^{(1)}\rangle + \langle\Psi_j^{(1)}|\varphi_k\rangle = 0$, which follows from (3.4). Thus,

$$M_{jk}^{(2)} = (i/\omega_{jk})\{\langle\varphi_j|P^{(1)}|\Psi_k^{(1)}\rangle + \langle\Psi_j^{(1)}|P^{(1)}|\varphi_k\rangle + \langle\varphi_j|P^{(2)}|\varphi_k\rangle\} - (i/\hbar\omega_{jk}^2)(E_j^{(1)} - E_k^{(1)})\langle\varphi_j|P^{(1)}|\varphi_k\rangle, \tag{3.24}$$

where we have used (3.20) for $\langle\varphi_j|\xi_k^{(1)}\rangle$.

We will not derive the explicit expressions for the diagonal matrix elements $\{M_{jj}^{(2)}\}$ since they do not enter into the expressions for the problems to be investigated in this paper; they can be obtained by using (A17) in the Appendix and other known quantities.

In actual numerical computations of the solutions of the TDPT, one only works with one set of potentials, usually the most convenient one for a particular field situation. It is therefore important first to establish the gauge invariance of all the quantities constructed from our procedure in the TDPT. Only after the gauge invariance is established can we be sure that the results obtained depend only on the prescribed fields and not on the particular potentials used. (When gauge invariance is not strictly maintained, the fields corresponding to the potentials used in the calculations may *differ* from the actual fields for a given physical situation. This interesting point has been recently investigated in detail by Leubner and Zoller (1980) and Leubner (1981).) Thus, let us first prove the gauge invariance of $M_{jk}^{(n)}$ before attempting to derive the expressions for the transition rates from (3.9)–(3.11).

### 3.4. *Gauge invariance of* $\{M_{jk}^{(n)}\}$

The proof of gauge invariance of the transition matrix elements $\{M_{jk}^{(n)}\}$consists in proving that

$$M_{jk}^{(n)}(\boldsymbol{A}', \Phi') = M_{jk}^{(n)}(\boldsymbol{A}, \Phi) \text{ for all } j \text{ and } k \text{ and all } n \geqslant 1. \tag{3.25}$$

Here, $\boldsymbol{A}'$ and $\Phi'$ are arbitrary potentials describing the fields $\boldsymbol{E}$ and $\boldsymbol{B}$ in (2.1); they are therefore related to $\boldsymbol{A}$ and $\Phi$ by the relation (A1) in the Appendix. As we explicitly illustrated in (3.25), $M_{jk}^{(n)}(\boldsymbol{A}', \Phi')$ are obtained by replacing $\boldsymbol{A}$ and $\Phi$ in $M_{jk}^{(n)}(\boldsymbol{A}, \Phi)$ by $\boldsymbol{A}'$ and $\Phi'$. That is, the relation (3.25) requires that the matrix elements $\{M_{jk}^{(n)}\}$ have the *same forms and same values in all gauges*, which is often referred to as *manifest gauge invariance*. (For a discussion of the concept of manifest gauge invariance, see Yang (1976), Cohen-Tannoudji *et al* (1977), Kobe and Smirl (1978), Leubner and Zoller (1980), Kobe and Yang (1980) and Leubner (1981).) For convenience of notation we shall use $M_{jk}^{\prime(n)}$ for $M_{jk}^{(n)}(\boldsymbol{A}', \Phi')$.

Since the proof of (3.25) requires consideration of potentials and power operators in the gauge of $(\boldsymbol{A}', \Phi')$, let us first construct in this new gauge the power operator $P'$ according to (2.4) and the first- and second-order power operators $P^{\prime(1)}$ and $P^{\prime(2)}$ according to (3.15) and (3.16). If we use $V_1' = -e(\boldsymbol{A}' \cdot \boldsymbol{p} + \boldsymbol{p} \cdot \boldsymbol{A}')/2mc$ and $V_2' = (e\boldsymbol{A}')^2/2mc^2$, then

$$P' = (e/2m)\{(\boldsymbol{p} - e\boldsymbol{A}'/c) \cdot \boldsymbol{E} + \boldsymbol{E} \cdot (\boldsymbol{p} - e\boldsymbol{A}'/c)\}, \tag{3.26}$$

$$P^{\prime(1)} \equiv \partial V_1'/\partial t + [H_0, e\Phi']/\mathrm{i}\hbar = e(\boldsymbol{p} \cdot \boldsymbol{E} + \boldsymbol{E} \cdot \boldsymbol{p})/2m = P^{(1)}, \tag{3.27}$$

$$P^{\prime(2)} \equiv \partial V_2'/\partial t + [V_1', e\Phi']/\mathrm{i}\hbar = -e^2 \boldsymbol{E} \cdot \boldsymbol{A}'/mc = P^{(2)} - e^2 \boldsymbol{E} \cdot \nabla\chi/mc. \tag{3.28}$$

That (3.25) is true for $n = 1$ can be seen as follows. According to (3.3), the *zeroth*-order eigenfunctions $\{\varphi_j\}$ are determined only by the 'unperturbed' Hamiltonian $H_0$. Hence, if we use $\{\Psi_j^{\prime(0)}\}$ for the zeroth-order eigenfunctions in the gauge of $(\boldsymbol{A}', \Phi')$, $\Psi_j^{\prime(0)} = \Psi_j^{(0)} = \varphi_j$. (For a degenerate case, the arguments leading to $\Psi_j^{\prime(0)} = \Psi_j^{(0)}$ are different.) Thus, (3.25) is true simply by (3.20) and (3.27) for $j \neq k$ and by (3.21) and the gauge invariance of $E_j^{(1)}$ for $j = k$. (From (3.19), one can also deduce the gauge invariance of $E_k^{(1)}$ since $\dot{E}_k^{(1)}$ is gauge invariant.)

The proof of (3.25) for $n = 2$ is more involved. Let us prove it here only for $j \neq k$. According to (3.24), $M_{jk}^{\prime(2)}$ is

$$\begin{aligned} M_{jk}^{\prime(2)} = (\mathrm{i}/\omega_{jk})\{&\langle\varphi_j|P^{\prime(1)}|\Psi_k^{\prime(1)}\rangle + \langle\Psi_j^{\prime(1)}|P^{\prime(1)}|\varphi_k\rangle + \langle\varphi_j|P^{\prime(2)}|\varphi_k\rangle \\ &- (\mathrm{i}/\hbar\omega_{jk}^2)(E_j^{\prime(1)} - E_k^{\prime(1)})\langle\varphi_j|P^{\prime(1)}|\varphi_k\rangle, \end{aligned} \tag{3.29}$$

where the primed quantities are obtained in $(\boldsymbol{A}', \Phi')$ in exactly the same manner as the unprimed quantities in $(\boldsymbol{A}, \Phi)$. If we use the choice of $\langle\varphi_j|\Psi_j^{(1)}\rangle$ as described in the Appendix and solve for $\Psi_j^{(1)}$, and do similarly for $\Psi_j'^{(1)}$, then it can be shown that

$$\Psi_k'^{(1)} = \Psi_k^{(1)} + \Lambda\varphi_k, \qquad \Lambda = ie\chi/c\hbar. \tag{3.30}$$

Finally, if we use the gauge invariance of $\{E_j^{(1)}\}$, $P'^{(1)} = P^{(1)}$ and (3.30) into (3.29), it can be shown from (3.24) and (3.29) that

$$\begin{aligned}(-i\omega_{jk})(M_{jk}'^{(2)} - M_{jk}^{(2)}) &= \langle\varphi_j|P^{(1)}|\Lambda\varphi_k\rangle + \langle\Lambda\varphi_j|P^{(1)}|\varphi_k\rangle + \langle\varphi_j|(P'^{(2)} - P^{(2)})|\varphi_k\rangle \\ &= 0.\end{aligned}$$

Finally, we mention that the gauge invariance of all higher-order transition matrix elements can be shown similarly by first choosing $\langle\varphi_j|\Psi_j^{(n)}\rangle$ to satisfy (A7).

In the next section, we will also use a single-frequency field to illustrate explicitly what we have proven here in terms of abstract symbols.

## 4. Perturbative rates of transitions

In this section, we shall apply the TDPT developed in § 3 to derive the first- and second-order net transition rates for a single-frequency external field. In order to illustrate explicitly the gauge invariance of the TDPT, we will specify *only the fields* and leave the expressions for the potentials to be arbitrary within the extent that they generate the specified fields. We shall show that our expressions for $M_{jk}^{(n)}$, although they are initially defined in terms of both potentials and fields, will eventually reduce to quantities that are *explicitly expressed only in terms of fields.* By doing this, we once again demonstrate that the TDPT formulated here does have the ability to eliminate the uncertainty in the construction of potentials from fields.

Because of the explicit demonstration of the gauge-invariance property, some procedures in § 3 will be repeated here. Although this repetition may look superfluous on the surface, it is essential for a deeper understanding of the basic properties of both the exact and the time-dependent perturbation theories of the gauge-invariant formulation.

### *4.1. Specification of fields and notation*

Let us now assume a single-frequency field with angular frequency $\omega$:

$$\boldsymbol{E}(\boldsymbol{r}, t) = \boldsymbol{E}_+(\boldsymbol{r})\, e^{i\omega t} + \boldsymbol{E}_-(\boldsymbol{r})\, e^{-i\omega t}, \qquad \boldsymbol{E}_+ = (\boldsymbol{E}_-)^*, \tag{4.1}$$

and similarly for $\boldsymbol{B}(\boldsymbol{r}, t)$, where * denotes the complex conjugate.

Since we have shown that the transition matrix elements $M_{jk}^{(n)}$ are manifestly gauge invariant, we may choose any arbitrary set of potentials to describe this field situation. For the purpose of demonstration, let us choose $\boldsymbol{A}$ and $\Phi$ to have the forms:

$$\boldsymbol{A}(\boldsymbol{r}, t) = \boldsymbol{A}_+(\boldsymbol{r})\, e^{i\omega t} + \boldsymbol{A}_-(\boldsymbol{r})\, e^{-i\omega t}, \qquad \boldsymbol{A}_+ = (\boldsymbol{A}_-)^*, \tag{4.2}$$

$$\Phi(\boldsymbol{r}, t) = \Phi_+(\boldsymbol{r})\, e^{i\omega t} + \Phi_-(\boldsymbol{r})\, e^{-i\omega t}, \qquad \Phi_+ = (\Phi_-)^*. \tag{4.3}$$

Here, $\boldsymbol{A}_\pm$ and $\Phi_\pm$ are left to be arbitrary except that they must combine to generate the correct fields,

$$\boldsymbol{E}_\pm = -\boldsymbol{\nabla}\Phi_\pm \mp (\mathrm{i}\omega/c)\boldsymbol{A}_\pm, \qquad \boldsymbol{A}_\pm = \mp(c/\mathrm{i}\omega)(\boldsymbol{E}_\pm + \boldsymbol{\nabla}\Phi_\pm), \tag{4.4}$$

and $\Phi_\pm(\boldsymbol{0}) = 0$ as required in the Appendix.

According to (3.19)–(3.21) and (3.24), $M^{(1)}_{jk}$ is linear in $\boldsymbol{E}$ and $M^{(2)}_{jk}$ is bilinear in the combination of $\boldsymbol{E}$ and $\boldsymbol{A}$. Let us now decompose them according to their frequency dependence.

$$M^{(1)}_{jk}(t) = M^{(1)}_{jk,+}\, \mathrm{e}^{\mathrm{i}\omega t} + M^{(1)}_{jk,-}\, \mathrm{e}^{-\mathrm{i}\omega t}, \tag{4.5}$$

$$M^{(2)}_{jk}(t) = M^{(2)}_{jk,+2}\, \mathrm{e}^{2\mathrm{i}\omega t} + M^{(2)}_{jk,0} + M^{(2)}_{jk,-2}\, \mathrm{e}^{-2\mathrm{i}\omega t}. \tag{4.6}$$

All other relevant operators, eigenvalue corrections, and perturbative eigenfunctions will be similarly decomposed according to their dependence on the potentials and/or fields. For example,

$$P^{(1)}_\pm = e(\boldsymbol{p}\cdot\boldsymbol{E}_\pm + \boldsymbol{E}_\pm\cdot\boldsymbol{p})/2m, \tag{4.7}$$

$$P^{(2)}_{\pm 2} = -e^2\boldsymbol{E}_\pm\cdot\boldsymbol{A}_\pm/mc = \hat{P}^{(2)}_{\pm 2} \pm (e^2/\mathrm{i}m\omega)\boldsymbol{E}_\pm\cdot\boldsymbol{\nabla}\Phi_\pm, \qquad \hat{P}^{(2)}_{\pm 2} = \pm(e\boldsymbol{E}_\pm)^2/m\mathrm{i}\omega, \tag{4.8}$$

$$V_{1,\pm} = -e(\boldsymbol{p}\cdot\boldsymbol{A}_\pm + \boldsymbol{A}_\pm\cdot\boldsymbol{p})/2mc = \pm(1/\mathrm{i}\omega)P^{(1)}_\pm \pm (1/\hbar\omega)[H_0, e\Phi_\pm]; \tag{4.9}$$

$$(\mathrm{i}e/c\hbar)F[\boldsymbol{A}_\pm] = \pm(1/\hbar\omega)F[-e\boldsymbol{E}_\pm] \mp (1/\hbar\omega)(e\Phi_\pm), \tag{4.10}$$

where $F$ has been defined in (A11).

### *4.2. Net transition rates*

If we substitute (4.5) and (4.6) into (3.10) and (3.11), the first-order net transition rates for the single-frequency excitation and de-excitation in which the particle makes a transition from the initial state i to the final state f are

$$T^{(1)}_{\mathrm{fi},\pm} = (2\pi/\hbar^2)|M^{(1)}_{\mathrm{fi},\pm}|^2\delta(\omega_{\mathrm{fi}} \pm \omega). \tag{4.11}$$

Similarly, the net transition rates for the double-frequency excitation and de-excitation are

$$T^{(2)}_{\mathrm{fi},\pm 2} = (2\pi/\hbar^2)|N^{(2)}_{\mathrm{fi},\pm 2}|^2\delta(\omega_{\mathrm{fi}} \pm 2\omega), \tag{4.12}$$

where

$$N^{(2)}_{\mathrm{fi},\pm 2} = -\sum_k \{M^{(1)}_{\mathrm{fk},\pm}[\hbar(\omega_{\mathrm{ki}} \pm \omega)]^{-1}M^{(1)}_{\mathrm{ki},\pm}\} + M^{(2)}_{\mathrm{fi},\pm 2}. \tag{4.13}$$

From (3.20) and (4.7), we get

$$M^{(1)}_{\mathrm{fi},\pm} = (\mathrm{i}/\omega_{\mathrm{fi}})\langle\varphi_{\mathrm{f}}|e(\boldsymbol{p}\cdot\boldsymbol{E}_\pm + \boldsymbol{E}_\pm\cdot\boldsymbol{p})/2m|\varphi_{\mathrm{i}}\rangle. \tag{4.14}$$

Note, according to (4.14) and (3.27), the first-order power operators *in all gauges* involve explicitly only the electric field. Hence, the question of whether different sets of potentials lead to different forms of the first-order power operators, and hence different first-order transition matrix elements, does *not* arise here. In order to demonstrate this point more clearly, let us put the potentials in (4.2) and (4.3) into (3.1), (3.4), (3.13) and (3.14) to evaluate $M^{(1)}_{\mathrm{fi}}$ directly without going through the procedure described in § 3.3. Since $\mathrm{f} \neq \mathrm{i}$, $M^{(1)}_{\mathrm{fi}} = \langle\varphi_{\mathrm{f}}|\xi^{(1)}_{\mathrm{i}}\rangle$. From (3.1) and (3.4),

$$\langle\varphi_{\mathrm{f}}|\Psi^{(1)}_{\mathrm{i}}\rangle = -(1/\hbar\omega_{\mathrm{fi}})\{\langle\varphi_{\mathrm{f}}|V_{1,+}|\varphi_{\mathrm{i}}\rangle\, \mathrm{e}^{\mathrm{i}\omega t} + \langle\varphi_{\mathrm{f}}|V_{1,-}|\varphi_{\mathrm{i}}\rangle\, \mathrm{e}^{-\mathrm{i}\omega t}\}, \tag{4.15}$$

where $V_{1,\pm}$ are defined in (4.9). From (3.13) and (4.15), and using the fact that $\varphi_f(\boldsymbol{r})$ is time-independent, it follows that

$$\langle\varphi_f|\xi_i^{(1)}\rangle = (1/\omega_{fi})\{\langle\varphi_f|(\omega_{fi}e\Phi_+ - \omega V_{1,+})|\varphi_i\rangle\, e^{i\omega t} + \langle\varphi_f|(\omega_{fi}e\Phi_- + \omega V_{1,-})|\varphi_i\rangle\, e^{-i\omega t}\}. \quad (4.16)$$

Furthermore,

$$\begin{aligned}\langle\varphi_f|\omega_{fi}e\Phi_\pm|\varphi_i\rangle &= (e/\hbar)\langle\varphi_f|[H_0, \Phi_\pm]|\varphi_i\rangle \\ &= (e/2mi)\langle\varphi_f|(\boldsymbol{p}\cdot\boldsymbol{\nabla}\Phi_\pm + \boldsymbol{\nabla}\Phi_\pm\cdot\boldsymbol{p})|\varphi_i\rangle. \end{aligned} \quad (4.17)$$

If we now use (4.4), (4.7), $V_{1,\pm}$ in (4.9), (4.16) and (4.17), it is trivially shown that

$$\langle\varphi_f|(\omega_{fi}e\Phi_\pm \mp \omega V_{1,\pm})|\varphi_i\rangle = i\langle\varphi_f|e(\boldsymbol{p}\cdot\boldsymbol{E}_\pm + \boldsymbol{E}_\pm\cdot\boldsymbol{p})/2m|\varphi_i\rangle,$$

which agrees exactly with the results obtained in § 3.3.

The first-order transition matrix elements in (4.14) have an interesting form under the dipole approximation $\boldsymbol{E}_\pm(\boldsymbol{r}) \approx \boldsymbol{E}_\pm(\boldsymbol{0})$ for transitions involving bound states. If we use this approximation for the field and the relation $\boldsymbol{p}/m = [\boldsymbol{r}, H_0]/i\hbar$, then

$$M_{fi,\pm}^{(1)} \approx (ie/\omega_{fi})\boldsymbol{E}_\pm(\boldsymbol{0})\cdot\langle\varphi_f|\boldsymbol{p}/m|\varphi_i\rangle = \langle\varphi_f|-e\boldsymbol{r}\cdot\boldsymbol{E}_\pm(\boldsymbol{0})|\varphi_i\rangle. \quad (4.18)$$

The procedure involved in demonstrating that the second-order transition matrix elements $M_{fi,\pm 2}^{(2)}$, which are initially defined in terms of potentials as can be seen from (3.24), can also be explicitly expressed in terms of fields only, is more involved as we shall show in the following subsection.

### *4.3. The second-order transition amplitudes $N_{fi,\pm 2}^{(2)}$*

To demonstrate that $M_{fi,\pm 2}^{(2)}$ can be explicitly expressed in fields only by starting from the potentials in (4.2) and (4.3), let us first list some useful relations that can be derived by using the procedure in § 3.1 and definitions in § 4.1. In the following, $k \neq i$, and $P_{\pm,ki}^{(1)} = \langle\varphi_k|P_\pm^{(1)}|\varphi_i\rangle$.

$$\begin{aligned}\langle\varphi_k|\Psi_{i,\pm}^{(1)}\rangle &= \mp(1/i\hbar\omega\omega_{ki})P_{\pm,ki}^{(1)} \mp (1/\hbar\omega)\langle\varphi_k|e\Phi_\pm|\varphi_i\rangle, \\ \langle\varphi_i|\Psi_{i,\pm}^{(1)}\rangle &= \pm\eta_{i,\pm}^{(1)}/\hbar\omega \mp (1/\hbar\omega)\langle\varphi_i|e\Phi_\pm|\varphi_i\rangle,\end{aligned}$$

and $P_{\pm,ff}^{(1)} = (\pm i\omega)E_{f,\pm}^{(1)}$. Thus, if we use $\Sigma_k''$ to denote the summation that *excludes* $k = i$ and f, then it can be shown that

$$\begin{aligned}&\{\langle\varphi_f|P^{(1)}|\Psi_i^{(1)}\rangle\}_{\pm 2} \\ &\quad = \mp(1/i\hbar\omega)\sum_k''\{P_{\pm,fk}^{(1)}(1/\omega_{ki})P_{\pm,ki}^{(1)}\} \mp (1/\hbar\omega)\langle\varphi_f|P_\pm^{(1)}(e\Phi_\pm)|\varphi_i\rangle \\ &\qquad + P_{\pm,fi}^{(1)}\{\eta_{i,\pm}^{(1)}/(\pm\hbar\omega) - E_{f,\pm}^{(1)}/(\hbar\omega_{fi})\}. \end{aligned} \quad (4.19)$$

Using a similar procedure, we get

$$\begin{aligned}&\{\langle\Psi_f^{(1)}|P^{(1)}|\varphi_i\rangle\}_{\pm 2} = \langle\Psi_{f,\mp}^{(1)}|P_\pm^{(1)}|\varphi_i\rangle \\ &\quad = \pm(1/i\hbar\omega)\sum_k''\{P_{\pm,fk}^{(1)}(1/\omega_{fk})P_{\pm,ki}^{(1)}\} \pm (1/\hbar\omega)\langle\varphi_f|(e\Phi_\pm)P_\pm^{(1)}|\varphi_i\rangle \\ &\qquad + P_{\pm,fi}^{(1)}\{-\eta_{f,\pm}^{(1)}/(\pm\hbar\omega) + E_{i,\pm}^{(1)}/\hbar\omega_{fi}\}. \end{aligned} \quad (4.20)$$

The two terms involving $e\Phi_\pm$ in (4.19) and (4.20) are the only gauge-dependent terms in

these two expressions. The operators of these two terms combine to give

$$(1/\hbar\omega)\{(e\Phi_\pm)P_\pm^{(1)} - P_\pm^{(1)}(e\Phi_\pm)\} = (e/\hbar\omega)[\Phi_\pm, P_\pm^{(1)}] = \mp(e^2/mi\omega)\boldsymbol{E}_\pm \cdot \nabla\Phi_\pm. \tag{4.21}$$

If we combine this result with the $P^{(2)}$ term in (3.24) and then use (4.8), the gauge-dependent terms in $M_{\mathrm{fi},\pm 2}^{(2)}$ disappear since

$$\langle\varphi_f|\{(1/\hbar\omega)(e\Phi_\pm P_\pm^{(1)} - P_\pm^{(1)} e\Phi_\pm) + P^{(2)}\}|\varphi_i\rangle = \hat{P}_{\pm 2,\mathrm{fi}}^{(2)}, \tag{4.22}$$

where the operators $\hat{P}_{\pm 2}^{(2)}$ are defined in (4.8).

From (3.24) and (4.19)–(4.22), we obtain $M_{\mathrm{fi},\pm 2}^{(2)}$ only in terms of gauge-invariant quantities:

$$\begin{aligned} M_{\mathrm{fi},\pm 2}^{(2)} = {} & \pm(\hbar/\omega\omega_{\mathrm{fi}})^{-1} \sum_k{}'' \{P_{\pm,fk}^{(1)} P_{\pm,ki}^{(1)} (1/\omega_{fk} - 1/\omega_{ki})\} \\ & + (\mathrm{i}/\omega_{\mathrm{fi}}) P_{\pm,\mathrm{fi}}^{(1)} \{(-\eta_{\mathrm{f},\pm}^{(1)} + \eta_{\mathrm{i},\pm}^{(1)})/(\pm\hbar\omega) - 2(E_{\mathrm{f},\pm}^{(1)} - E_{\mathrm{i},\pm}^{(1)})/\hbar\omega_{\mathrm{fi}}\} \\ & + (\mathrm{i}/\omega_{\mathrm{fi}}) \hat{P}_{\pm 2,\mathrm{fi}}^{(2)}. \end{aligned} \tag{4.23}$$

Thus, we have demonstrated that despite our deliberate choice of the arbitrary potentials in (4.2) and (4.3), $M_{\mathrm{fi},\pm 2}^{(2)}$ depend only on the fields. (Let us note that the gauge invariance of $\{E_j^{(n)}\}$ implies that they are determined only by the *magnetic* field. This is because if $\nabla \times \boldsymbol{A} = 0$, then it can be shown that $E_j^{(n)} = 0$ for all $j$ and all $n \geqslant 1$ (e.g. Yang 1977).)

Finally, from (3.20), (3.21), (4.13) and (4.23), and after a very lengthy algebraic procedure, we get the expression for $N_{\mathrm{fi},\pm 2}^{(2)}$ as follows.

$$\begin{aligned} N_{\mathrm{fi},\pm 2}^{(2)} = {} & \sum_k{}'' P_{\pm,fk}^{(1)} [\hbar(\mp\omega_{\mathrm{fi}}/2)(\omega_{ki} \pm \omega)]^{-1} P_{\pm,ki}^{(1)} \\ & + (2/\mathrm{i}\omega_{\mathrm{fi}}) P_{\pm,\mathrm{fi}}^{(1)} \{E_{\mathrm{f},\pm}^{(1)}/[\hbar(\omega_{\mathrm{fi}} \pm \omega)] + E_{\mathrm{i},\pm}^{(1)}/(\pm\hbar\omega)\} \\ & + (\mathrm{i}/\omega_{\mathrm{fi}}) \hat{P}_{\pm 2,\mathrm{fi}}^{(2)} + (\omega_{\mathrm{fi}} \pm 2\omega)\Delta_{\mathrm{fi},\pm 2}^{(2)}, \end{aligned} \tag{4.24}$$

where

$$\begin{aligned} \Delta_{\mathrm{fi},\pm 2}^{(2)} = {} & \sum_k{}'' P_{\pm,fk}^{(1)} [\hbar\omega\omega_{\mathrm{fi}}\omega_{fk}(\omega_{ki} \pm \omega)]^{-1} P_{\pm,ki}^{(1)} + (\mathrm{i}\hbar\omega_{\mathrm{fi}}^2)^{-1} P_{\pm,\mathrm{fi}}^{(1)} \{E_{\mathrm{f},\pm}^{(1)}/(\omega_{\mathrm{fi}} \pm \omega) - E_{\mathrm{i},\pm}^{(1)}/(\pm\omega)\} \\ & + [\mathrm{i}\hbar\omega_{\mathrm{fi}}(\pm\omega)(\omega_{\mathrm{fi}} \pm \omega)]^{-1} P_{\pm,\mathrm{fi}}^{(1)} \eta_{\mathrm{f},\pm}^{(1)}. \end{aligned} \tag{4.25}$$

This ends our investigation of the first- and second-order perturbative rates of transitions. Higher-order rates can be obtained by the same procedure, although it will be very tedious. In the following section, we shall compare our results with the conventional results.

## 5. Comparison with the conventional results

In this section, we shall compare the rates of transition derived in the previous section with those derived from the conventional time-dependent perturbation theory. We will see that for the first- and second-order transition rates, the gauge-invariant and conventional results agree exactly. After the comparison, we will mention one characteristic difference between these two formulations in the *approximate* wavefunctions.

In the conventional formulation, the wavefunction $\Psi(\boldsymbol{r}, t)$ is expanded in the basis set of eigenfunctions of the 'unperturbed' Hamiltonian, resulting in the expansion

coefficients $\{c_j(t)\}$:

$$\Psi(\boldsymbol{r}, t) = \sum_j c_j(t)\varphi_j(\boldsymbol{r}) \exp(-\mathrm{i}\omega_j t), \tag{5.1}$$

where $\hbar\omega_j$ and $\varphi_j(\boldsymbol{r})$ are respectively an eigenvalue and the associated eigenfunction of the 'unperturbed' Hamiltonian. If we write

$$c_j(t) = \sum_n c_j^{(n)}(t)$$

then these coefficients $\{c_j^{(n)}(t)\}$ satisfy equations (3.9)–(3.11) with $M_{jk}^{(n)}$, $n = 1$ and 2, replaced by the matrix elements $\tilde{V}_1$ and $\tilde{V}_2$ in the basis functions $\{\varphi_j(\boldsymbol{r})\}$. Here, $\tilde{V}_1$ and $\tilde{V}_2$ are

$$\tilde{V}_1 = -e(\boldsymbol{p}\cdot\tilde{\boldsymbol{A}} + \tilde{\boldsymbol{A}}\cdot\boldsymbol{p})/2mc, \qquad \tilde{V}_2 = (e\tilde{\boldsymbol{A}})^2/2mc^2, \tag{5.2}$$

where we have chosen the gauge for the fields in (4.1) to be (the conventional choice of the radiation gauge (e.g. Sakurai 1967))

$$\tilde{\boldsymbol{A}}(\boldsymbol{r}, t) = \tilde{\boldsymbol{A}}_+(\boldsymbol{r})\,\mathrm{e}^{\mathrm{i}\omega t} + \tilde{\boldsymbol{A}}_-(\boldsymbol{r})\,\mathrm{e}^{-\mathrm{i}\omega t}, \qquad \tilde{\Phi} = 0. \tag{5.3}$$

Since this set of potentials is to generate the fields in (4.1), it follows that

$$\boldsymbol{E}_\pm(\boldsymbol{r}) = \mp(\mathrm{i}\omega/c)\tilde{\boldsymbol{A}}_\pm(\boldsymbol{r}) \quad \text{or} \quad \tilde{\boldsymbol{A}}_\pm(\boldsymbol{r}) = \mp(c/\mathrm{i}\omega)\boldsymbol{E}_\pm(\boldsymbol{r}). \tag{5.4}$$

Hence,

$$\tilde{V}_{1,\pm} = \pm(1/\mathrm{i}\omega)P_\pm^{(1)}, \qquad \tilde{V}_{2,\pm 2} = \mp(\mathrm{i}/2\omega)\hat{P}_{\pm 2}^{(2)}, \tag{5.5}$$

where $P_\pm^{(1)}$ and $\hat{P}_{\pm 2}^{(2)}$ are defined in (4.7) and (4.8).

The conventional single- and double-frequency rates of transitions are

$$\tilde{T}_{\mathrm{fi},\pm}^{(1)} = (2\pi/\hbar^2)|\tilde{V}_{1,\pm;\mathrm{fi}}|^2\delta(\omega_{\mathrm{fi}} \pm \omega), \tag{5.6}$$

$$\tilde{T}_{\mathrm{fi},\pm 2}^{(2)} = (2\pi/\hbar^2)|\tilde{N}_{\mathrm{fi},\pm 2}^{(2)}|^2\delta(\omega_{\mathrm{fi}} \pm 2\omega), \tag{5.7}$$

where $\tilde{V}_{1,\pm;\mathrm{fi}} = \langle\varphi_{\mathrm{f}}|\tilde{V}_{1,\pm}|\varphi_{\mathrm{i}}\rangle$ and

$$\tilde{N}_{\mathrm{fi},\pm 2}^{(2)} = -\sum_k \{\tilde{V}_{1,\pm;\mathrm{f}k}[\hbar(\omega_{k\mathrm{i}} \pm \omega)]^{-1}\tilde{V}_{1,\pm;k\mathrm{i}}\} + \tilde{V}_{2,\pm 2;\mathrm{fi}} \tag{5.8}$$

where $\tilde{V}_{2,\pm 2;\mathrm{fi}} = \langle\varphi_{\mathrm{f}}|\tilde{V}_{2,\pm 2}|\varphi_{\mathrm{i}}\rangle$.

From (3.20) and (5.4), it is obvious that

$$M_{\mathrm{fi},\pm}^{(1)} = \mp(\omega/\omega_{\mathrm{fi}})\tilde{V}_{1,\pm;\mathrm{fi}}. \tag{5.9}$$

Furthermore, if we use $\tilde{V}_{1,\pm;jj} = E_{j,\pm}^{(1)}$ and (5.4), then it can be shown that

$$\tilde{N}_{\mathrm{fi},\pm 2}^{(2)} = \sum_k{}'' P_{\pm,\mathrm{f}k}^{(1)}[\hbar\omega^2(\omega_{k\mathrm{i}} \pm \omega)]^{-1}P_{\pm,k\mathrm{i}}^{(1)} + (\mp\mathrm{i}\omega)^{-1}P_{\pm,\mathrm{fi}}^{(1)}\{E_{\mathrm{f},\pm}^{(1)}/[\hbar(\omega_{\mathrm{fi}} \pm \omega)] + E_{\mathrm{i},\pm}^{(1)}/(\pm\hbar\omega)\}$$
$$+ [\mathrm{i}/(\mp 2\omega)]\hat{P}_{\pm 2;\mathrm{fi}}^{(2)} \tag{5.10}$$

where the double prime in the summation means excluding $k = \mathrm{i}$ and f. Comparing (5.7) with (4.24), we see that

$$N_{\mathrm{fi},\pm 2}^{(2)} = \mp(2\omega/\omega_{\mathrm{fi}})\tilde{N}_{\mathrm{fi},\pm 2}^{(2)} + (\omega_{\mathrm{fi}} \pm 2\omega)\Delta_{\mathrm{fi},\pm 2}^{(2)}. \tag{5.11}$$

Because of the presence of $\delta(\omega_{\mathrm{fi}} \pm n\omega)$, $n = 1$ and 2, in the expressions for the net transition rates in (4.11), (4.12), (5.5) and (5.6), we see that the conventional and the gauge-invariant *perturbative* net transition rates agree completely.

Let us now discuss one important characteristic difference in the approximate wavefunctions obtained from these two formulations. Assume that we have a first-order absorption with $\omega_{fi} = \omega$. The only dominant coefficients are $c_i^{(0)}(t)$ and $c_{f,-}^{(1)}(t)$ in the conventional formulation and are $b_i^{(0)}(t)$ and $b_{f,-}^{(1)}(t)$ in the gauge-invariant formulation. Since equation (3.9) is satisfied by both $c_i^{(0)}(t)$ and $b_i^{(0)}(t)$, let us set $c_i^{(0)}(t) = b_i^{(0)}(t) = 1$ without loss of generality. Because $\omega$ is exactly equal to $\omega_{fi}$, we have $b_{f,-}^{(1)}(t) = c_{f,-}^{(1)}(t)$.

According to (5.1), the conventional formulation will give the dominant terms of the wavefunction as

$$\Psi(r, t) \approx \varphi_i(r) \exp(-i\omega_i t) + c_{f,-}^{(1)}(t)\varphi_f(r) \exp(-i\omega_f t). \tag{5.12}$$

On the other hand, the approximate wavefunction from the gauge-invariant formulation is, according to (3.14),

$$\Psi(r, t) \approx \exp(-i\omega_i t)\Big\{\varphi_i(r) + \sum_{m=1}^{\infty} \Psi_i^{(m)}(r, t)\Big\}$$
$$+ b_{f,-}^{(1)}(t) \exp(-i\omega_f t)\Big\{\varphi_f(r) + \sum_{m=1}^{\infty} \Psi_f^{(m)}(r, t)\Big\}. \tag{5.13}$$

Thus, despite the fact that $c_{f,-}^{(1)}(t)$ is identical to $b_{f,-}^{(1)}(t)$, the two *approximate* wavefunctions are different.

## 6. Discussions

The fact that the conventional interpretation of the quantum mechanical probability amplitudes and probabilities is gauge dependent has long been suspected by Lamb (1952) and Power and Zienau (1959) through their investigations of *approximate* solutions to the time-dependent Schrödinger equation (with decay constants added phenomenologically). Their suspicion is recently confirmed by the theoretical investigations of the *exact* probability amplitudes and probabilities by this author (Yang 1976, 1982), Kobe and Smirl (1978), Kobe and Wen (1980) and Leubner and Zoller (1980). It can also be (indirectly) understood from a very detailed examination of the gauge dependence of the conventional interaction Hamiltonians and their matrix elements in the basis set of eigenfunctions of the 'unperturbed' Hamiltonian recently given by Power (1978) and Power and Thirunamachandran (1978). But, the simplest way to understand this subject on a fundamental level is the discussion of Cohen-Tannoudji *et al* (1977) on the subject of true physical and non-physical quantities. One very important result of their discussion is that $p^2/2m$ *in general* represents a *non-physical* quantity.

In contrast, our formulation as briefly described in § 2 is *manifestly* gauge invariant and consistent with the Foldy–Wouthuysen transformations when applied to the relativistic (Dirac) and non-relativistic quantum mechanics (Yang 1982).

Because of the above, it is important to compare some *approximate* results from these two different formulations. Here, we have chosen the perturbative results for the obvious reason that they are the most often-used approximate results to compare with experiment. We have seen that the first- and second-order net transition rates computed from the conventional and the gauge-invariant TDPT's agree completely.

The comparison of these two perturbative rates of transition has two important implications. First, we now understand that the conventional *perturbative* rates of transition are indeed gauge invariant despite the fact that the exact formulation is gauge dependent. Second, we also learn that the gauge-invariant formulation can reproduce some conventional results under some approximations. The latter is important in practice since it is the conventional perturbative results that have been tested against experiment.

Although the first- and second-order transition rates from these two formulations agree, in general the transition probability amplitudes and transition probabilities do not. This is especially true when the transition amplitudes can be evaluated exactly. It is precisely because of this difference in the conventional and the gauge-invariant transition amplitudes that the gauge-invariant formulation can resolve some apparent gauge-related paradoxes in the interpretation of quantum mechanics, as explained in detail recently by Leubner and Zoller (1980).

## Acknowledgments

The author is grateful to the Nuclear Theory Group of the University of Maryland, College Park, especially to Dr M K Banerjee, Dr J J Griffin, Dr E F Redish and Dr S Wallace, for the hospitality, encouragement and helpful discussions, and to Dr D H Kobe for helpful discussions. He also acknowledges financial support from the National Science Foundation and the US Energy Research and Development Administration (1975–77) and from the National Science Foundation and the University of Wisconsin–Madison Graduate School Research Council (1980–81).

## Appendix. Normalisation of perturbative eigenfunctions

In this Appendix, we will briefly discuss a simple method of choosing the values of $\delta_j^{(n)} \equiv \langle \varphi_j | \Psi_j^{(n)} \rangle$, $n \geq 1$, to satisfy (3.7) and the required properties under gauge transformations. For this purpose, we must also consider a different gauge with potentials $\boldsymbol{A}'$ and $\Phi'$ that are related to $\boldsymbol{A}$ and $\Phi$ in (2.1) by an arbitrary gauge function $\chi(\boldsymbol{r}, t)$ by

$$\boldsymbol{A}' = \boldsymbol{A} + \boldsymbol{\nabla}\chi, \qquad \Phi' = \Phi - (1/c)\,\partial\chi/\partial t. \tag{A1}$$

In this new gauge, the Hamiltonian $H'$, the energy operator $H'_B$, and the interaction operators $V'_1$ and $V'_2$ to be used in the Rayleigh–Schrödinger time-independent perturbation theory are:

$$H' = (\boldsymbol{p} - e\boldsymbol{A}'/c)^2/2m + eV_0 + e\Phi', \tag{A2}$$

$$H'_B = (\boldsymbol{p} - e\boldsymbol{A}'/c)^2/2m + eV_0 = H_0 + V'_1 + V'_2, \tag{A3}$$

where $H_0 = \boldsymbol{p}^2/2m + eV_0$, and

$$V'_1 = -e(\boldsymbol{A}' \cdot \boldsymbol{p} + \boldsymbol{p} \cdot \boldsymbol{A}')/2mc, \qquad V'_2 = (e\boldsymbol{A}')^2/2mc^2. \tag{A4}$$

The operators $H_B$ in (3.1) and $H'_B$ in (A3) are related by

$$H'_B = \exp(\Lambda) H_B \exp(-\Lambda), \qquad \Lambda = ie\chi/c\hbar. \tag{A5}$$

If we use $\{\Psi'_j(\boldsymbol{r}, t)\}$ to denote the *exact* eigenfunctions of $H'_B$, then (A5) implies that they

are related to the eigenfunctions $\{\Psi_j(\boldsymbol{r}, t)\}$ of $H_B$ by

$$\Psi_j'(\boldsymbol{r}, t) = \exp(\Lambda)\Psi_j(\boldsymbol{r}, t). \tag{A6}$$

Let us now use $\Psi_j^{\prime(n)}$ to denote the $n$th-order eigenfunction correction of $j$th state obtained by the RSTIPT. In order that these $\{\Psi_j^{\prime(n)}\}$ have the correct behaviour under gauge transformation, they must be related to $\{\Psi_j^{(n)}\}$ in (3.2)–(3.7) by the perturbative equivalent of (A6), which takes the form

$$\Psi_j^{\prime(n)} = \sum_{m=0}^{n} (\Lambda^m/m!)\Psi_j^{(n-m)} \qquad \text{or} \qquad \Psi_j^{(n)} = \sum_{m=0}^{n} [(-\Lambda)^m/m!]\Psi_j^{\prime(m)}. \tag{A7}$$

If we set $n = 1$, take the projection onto $\varphi_j$, and denote $\langle\varphi_j|\Psi_j^{\prime(1)}\rangle$ by $\delta_j^{\prime(1)}$, then

$$\delta_j^{\prime(1)} - \delta_j^{(1)} = (\mathrm{i}e/c\hbar)\langle\varphi_j|\chi(\boldsymbol{r}, t)|\varphi_j\rangle. \tag{A8}$$

As is clear from (A8), the usual intermediate normalisation $\langle\varphi_j|\Psi_j^{(n)}\rangle = 0$ for all $n \geq 1$ (e.g. Messiah 1966) must not be used for all gauges.

Before we discuss the detail of how to 'solve' (A8), let us first set up a uniform standard. From now on, we shall require that *all scalar potentials* vanish at the origin at all times. If the scalar potential in $(\boldsymbol{A}, \Phi)$ does not satisfy this requirement, we simply do the substitution: $\Phi(\boldsymbol{r}, t) \to \Phi(\boldsymbol{r}, t) - \Phi(\boldsymbol{0}, t)$. As is clear from (2.1) and (2.9), such a requirement affects neither the exact or approximate fields nor the transition matrix elements between different states. (It simply shifts the phases of all $a_j(t)$ by the same amount.) Once the scalar potentials are required to have this behaviour, we may further assume that all gauge functions $\chi(\boldsymbol{r}, t)$ vanish at the origin at all times.

We now wish to solve (A8) in the form:

$$\langle\varphi_j|\chi(\boldsymbol{r}, t)|\varphi_j\rangle = \langle\varphi_j|F[\boldsymbol{A}']|\varphi_j\rangle - \langle\varphi_j|F[\boldsymbol{A}]|\varphi_j\rangle, \tag{A9}$$

where $F[\boldsymbol{A}']$ is a function of $\boldsymbol{A}'$ only. Note that the right-hand side requires that the two terms be obtained in an *identical* manner. To find $F$, we use the condition that $\chi(\boldsymbol{0}, t) = 0$ to write

$$\chi(\boldsymbol{r}, t) = \int_{\boldsymbol{0}}^{\boldsymbol{r}} \mathrm{d}\boldsymbol{s} \cdot \boldsymbol{\nabla}\chi(\boldsymbol{s}, t) = \int_{\boldsymbol{0}}^{\boldsymbol{r}} \mathrm{d}\boldsymbol{s} \cdot [\boldsymbol{A}'(\boldsymbol{s}, t) - \boldsymbol{A}(\boldsymbol{s}, t)] \tag{A10}$$

along any path from $\boldsymbol{0}$ to $\boldsymbol{r}$ since $\boldsymbol{\nabla} \times (\boldsymbol{A}' - \boldsymbol{A}) = 0$.

The simplest way of casting (A10) into the form of (A9) is to use one existing technique associated with the *multipolar* gauge (e.g. Power and Zienau 1959, Fiutak 1963, Woolley 1975) and to choose $\boldsymbol{s} = u\boldsymbol{r}$ with $0 \leq u \leq 1$. Thus, we 'solve' (A9) by

$$F[\boldsymbol{A}] = \int_0^1 \mathrm{d}u\, \boldsymbol{r} \cdot \boldsymbol{A}(u\boldsymbol{r}, t). \tag{A11}$$

With this choice, $\delta_j^{(1)}$ is†

$$\delta_j^{(1)} = (\mathrm{i}e/c\hbar)\langle\varphi_j|F[\boldsymbol{A}]|\varphi_j\rangle. \tag{A12}$$

Using this definition of $F$, we can also show that

$$\langle\varphi_j|e\Phi|\varphi_j\rangle + \langle\varphi_j|-\mathrm{i}\hbar\,\partial\Psi_j^{(1)}/\partial t\rangle = \langle\varphi_j|F[-e\boldsymbol{E}]|\varphi_j\rangle, \tag{A13}$$

which will appear in the time-dependent perturbation theory in § 3. Note, $F[-e\boldsymbol{E}]$

† One would prefer having a procedure that can *uniquely* determine $\delta_j^{(1)}$. However, in the absence of such a procedure, one resorts to a choice.

agrees exactly with the scalar potential in the multipolar gauge. Finally, we note that $\delta_j^{(1)}$ is purely imaginary so that (3.7) for $n = 1$ is satisfied.

Let us briefly describe how to 'solve' for $\delta_j^{(2)}$ that will satisfy (3.7) for $n = 2$. From (A7), we get two results:

$$\delta_j'^{(2)} - \delta_j^{(2)} = \langle\varphi_j|\Lambda|\Psi_j^{(1)}\rangle + \tfrac{1}{2}\langle\varphi_j|\Lambda^2|\varphi_j\rangle, \tag{A14}$$

$$\delta_j^{(2)} - \delta_j'^{(2)} = -\langle\varphi_j|\Lambda|\Psi_j'^{(1)}\rangle + \tfrac{1}{2}\langle\varphi_j|\Lambda^2|\varphi_j\rangle. \tag{A15}$$

From these two results, we get

$$\delta_j'^{(2)} - \delta_j^{(2)} = \tfrac{1}{2}\{\langle\varphi_j|\Lambda|\Psi_j^{(1)}\rangle + \langle\varphi_j|\Lambda|\Psi_j'^{(1)}\rangle\}. \tag{A16}$$

This relation can eventually be manipulated into a form (with the help of the relation $\Psi_j'^{(1)} = \Psi_j^{(1)} + \Lambda\varphi_j$ and (A9)) so that one can 'solve' for $\delta_j^{(2)}$ with the explicit expression:

$$\delta_j^{(2)} = -\tfrac{1}{2}\langle\Psi_j^{(1)}|\Psi_j^{(1)}\rangle + (ie/2c\hbar)\{\langle\varphi_j|\boldsymbol{F}[\boldsymbol{A}]|\Psi_j^{(1)}\rangle + \langle\Psi_j^{(1)}|\boldsymbol{F}[\boldsymbol{A}]|\varphi_j\rangle\}. \tag{A17}$$

We will stop here as the procedure for deriving the higher order $\delta_j^{(n)}$ will be exceedingly complicated, although the basic idea is the same.

## References


Bohr N 1928 *Nature* **121** 580
Cohen-Tannoudji C, Diu B and Laloë F 1977 *Quantum Mechanics* (Paris: Hermann/Wiley) pp 315–28
Fiutak J 1963 *Can. J. Phys.* **41** 12
Foldy L L and Wouthuysen S A 1950 *Phys. Rev.* **78** 29
Jackson J D 1975 *Classical Electrodynamics* 2nd edn (New York: Wiley) pp 236–41
Kobe D H and Smirl A L 1978 *Am. J. Phys.* **46** 624
Kobe D H and Wen E C-T 1980 *Phys. Lett.* **80A** 121
Kobe D H and Yang K-H 1980 *J. Phys. A: Math. Gen.* **13** 3171
Lamb W E Jr 1952 *Phys. Rev.* **85** 259
Langhoff P, Epstein S T and Karplus M 1972 *Rev. Mod. Phys.* **44** 602
Leubner C 1981 *Am. J. Phys.* **49** 738
Leubner C and Zoller P 1980 *J. Phys. B: At. Mol. Phys.* **13** 3613
Merzbacher A 1961 *Quantum Mechanics* (New York: Wiley) ch 19
Messiah A 1966 *Quantum Mechanics* (Amsterdam: North-Holland/Wiley) ch XVI
Power E A 1978 in *Multiphoton Processes* ed J H Eberly and P Lambropoulos (New York: Wiley) p 11
Power E A and Thirunamachandran T 1978 *Am. J. Phys.* **46** 370
Power E A and Zienau S 1959 *Phil. Trans. R. Soc.* A **251** 427
Sakurai J J 1967 *Advanced Quantum Mechanics* (Reading, MA: Addison-Wesley) ch 2
Woolley R G 1975 *Adv. Chem. Phys.* **33** 153
Yang K-H 1976 *Ann. Phys., NY* **101** 62
—— 1977 *University of Maryland, technical report* No 78-012
—— 1981 *Phys. Lett.* **84A** 165
—— 1982 *J. Phys. A: Math. Gen.* **15** 437