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Questions of gauge and basis sets for the representation of electromagnetic interactions in quantum mechanics

S. Olariu and Iovitzu Popescu
Central Institute of Physics, Bucharest/Magurele, Romania

C. B. Collins
Center for Quantum Electronics, The University of Texas at Dallas, Box 688, Richardson, Texas 75080
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Recent concerns about the gauge dependence of transition amplitudes describing the changes of state of quantized systems interacting with electromagnetic radiations have led to the development of invariant schemes for the expression of the time-dependent quantities involved. It is shown in this work that such schemes are not uniquely specified by the requirement for gauge invariance. Moreover, they simply exchange a dependence upon the gauge of the electromagnetic potentials for a previously unrecognized dependence upon the representation of basis states describing initial and final states of the process that is equivalent to a dependence upon gauge. However, general expressions are developed in this work which show that resonant transitions which correspond to physically observable processes involving the pure or mixed absorption and emission of N photons are gauge invariant regardless of the multipolarity of the transition moments and independent of the representation of the basis states of the system. A preferred representation is introduced which is shown to accommodate the physical effects generally encountered.

INTRODUCTION

In 1931, Göppert-Mayer[1] introduced an expression for the second-order transition probability for the interactions of a charged system with electromagnetic radiation that consisted of sums of products of matrix elements describing sequences of nonresonant single-photon transitions through intermediate states connected to the initial and final states by interactions involving the time-varying electric field. It corresponded in form to the result obtained from second-order perturbation theory for transitions between the stationary states of a quantal system when the transition is mediated by the operator

$$\hat{H}_{\text{int}} = -e\vec{\mathrm{E}}\cdot\vec{\mathrm{r}}\,, \tag{1}$$

where $\vec{\mathrm{r}}$ is the spatial coordinate of a particle of charge e in an electric field $\vec{\mathrm{E}}$ which may be time and space dependent. In a subsequent reformulation the interaction Hamiltonian was expressed in terms of the electromagnetic potentials Φ and $\vec{\mathrm{A}}$ so that

$$\hat{H}_{\text{int}} = -(e/Mc)\vec{\mathrm{A}}\cdot\vec{\mathrm{p}}\,, \tag{2}$$

where $\vec{\mathrm{p}}$ was the operator for the momentum of the charge. Although not immediately recognized, this implicitly introduced serious complications concerning the invariance of calculated results to arbitrary choices of the gauges of the fields and to selections of basis sets of states describing the material systems. Apparently the pervasive nature of the consequences was recognized[2] only as recently as 1972.

Kobe and Smirl[3] reviewed these difficulties in 1978 showing that the change of gauge of the electromagnetic interaction mediating a *resonant* second-order transition between states belonging to a basis set describing a material system in a *field-free* space could introduce a change in the computed transition rate of the order of $(\omega_1/\omega_2)^2$ where the ω represented the frequencies of the radiation fields inducing the transitions to and from the intermediate state, respectively. For example, because of the large ratio of photon frequencies, recent calculations of the rates at which optical fields induce the absorption of γ radiations[4] have shown changes in the transition probabilities as great as 10^{10} to result from changes of gauge in certain approximations.

In general the second-order transition probabilities must be summed over all possible intermediate states and for that case Kobe[5] has shown that the resulting sum is gauge invariant for any complete basis set. The extreme divergence observed between specific calculations employing representations (1) and (2) result from the fact that the sums obtained from the more frequently used expression, Eq. (2), are poorly convergent and undergo oscillation at large amplitude when only a few terms are used. Bassani *et al.*[6] have shown in detailed calculations that convergence nevertheless occurs to the same value obtained more rapidly with the interaction given by Eq. (1) if all intermediate states, including continua, are considered.

While this resolved the principal obstructions encountered in the mechanics of computing transition rates, conceptual ambiguities were introduced which made difficult the choice of basis sets of functions describing the stationary states of the material system interacting with the radiation.

Generally, the lowest order of interaction of a charged system with electromagnetic radiation is the minimum in the number of photons N

$$N=\sum_i (m_i+n_i)\,, \tag{3}$$

required for the conservation of energy

$$E_f-E_0=\sum_i (n_i-m_i)\hbar\omega_i\,, \tag{4}$$

where E_0 and E_f are the quantized energies of the material system in its initial and final states, respectively, and n_i and m_i represent the number of photons of frequency ω_i absorbed and emitted, respectively, during the transition. Equation (4) implies that to the order N the transition is *resonant*, and hence from the uncertainty principle, represents the creation of a final state f having a lifetime sufficiently long to permit physical measurement. As mentioned above, for $N=2$ such transitions were demonstrated by Kobe[5] to be gauge invariant. However, that work also showed that the probabilities of *nonresonant* transitions of order $N\leq 2$ were gauge dependent if the basis set of functions employed in the calculations was not carefully selected. The most transparent example perhaps is the case of the nonresonant absorption of single photons discussed by Kobe and Smirl.[3] They showed it to be necessary to include part of the electromagnetic potentials describing the interaction in the description of the basis functions.

For a nonrelativistic charged particle without spin subject to a static potential $U(\vec{r})$ and interacting with an external radiation field described semiclassically by the electromagnetic potentials $\phi(\vec{r},t)$ and $\vec{A}(\vec{r},t)$ the Hamiltonian of the system is

$$\hat{H}(t)=\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2+U+e\phi\,, \tag{5a}$$

where $\hat{H}$ and $\vec{p}$ are operators, and the basis states of the particle are defined by the basis Hamiltonian in the most general form

$$\hat{H}_B=\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2+U+e\phi_0(\vec{r},t)\,, \tag{5b}$$

where ϕ_0 is a potential which defines the basis states Ψ_i through the eigenvalue relation

$$\hat{H}_B\Psi_i=E_i\Psi_i\,. \tag{5c}$$

Previously Yang[7] had observed that the use of a basis-defining Hamiltonian equivalent to (5b) with $\phi_0=0$ resulted in the development of transition amplitudes which were gauge invariant, as later did Kobe and Smirl.[3] The consequent result was that the description of nonresonant transitions required the use of initial and final states whose composition depended upon a part of the electromagnetic field providing the interaction, that part being determined by the requirement for gauge invariance of the nonresonant transition probabilities.

It will be shown in this work that the requirement of gauge invariance is insufficient to uniquely define the basis set of states describing the material system and that the choice made by Yang[7] actually precludes the description of certain realistic systems. A generalized form of the basis set is examined in this work and its configuration in terms of the physical fields is recommended. In particular, it is shown that $e\phi_0$ is best represented by the energy of the interaction of the particle with the radiation fields

$$e\phi_0=-e\vec{E}\cdot\vec{r}-\vec{\mu}\cdot\vec{H}\,. \tag{6}$$

Moreover, an examination of the nonresonant transition probabilities introduced by Kobe[5] shows them to be without a clear physical interpretation that necessitates gauge invariance. It is shown in the work reported here that, whereas resonant transitions of order N are always gauge invariant, the component nonresonant intermediate steps of order less than N are naturally dependent upon both gauge and the basis of representation as a result of the nonphysical nature of the intermediate states. Rather than make a choice of gauge and basis set to give unnecessary invariance to the nonresonant transitions, it is shown to be more consistent with physical reality to adopt a basis set defined by Eq. (6), where the $e\phi_0$ represents the envelope of the physical fields, thus accommodating the Stark effect precluded by Yang,[7] and to represent the interaction potential also by the physical fields. *A posteriori*, the original representation suggested by Göppert-Mayer[1] is found more closely adherent to physical reality. The lack of gauge invariance found to result for the nonresonant transitions to the intermediate states in some representations of the basis states is shown to be canceled by any subsequent and additional nonresonant step required to bring about a final transition which becomes physically observable by virtue of being resonant to a higher order.

GAUGE INVARIANCE IN CLASSICAL AND QUANTUM MECHANICS

If the electromagnetic fields $\vec{E},\vec{B}$ are expressed in terms of the potentials $\phi,\vec{A}$

$$\vec{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}\,, \tag{7a}$$

$$\vec{B} = \nabla \times \vec{A}\,, \tag{7b}$$

those potentials are not uniquely specified by the physical fields. If f is any continuous function of space and time, new potentials

$$\phi' = \phi - \frac{1}{c}\frac{\partial f}{\partial t}\,, \tag{8a}$$

$$\vec{A}' = \vec{A} + \nabla f \tag{8b}$$

give the same electromagnetic fields and the same forces on elementary charges

$$\vec{F} = e\left(\vec{E} + \frac{\vec{v}}{c} \times \vec{B}\right), \tag{9}$$

since the forces are expressed directly in terms of the fields. The independence of the resulting motion from the nature of the function f represents the gauge invariance of classical mechanics.

In quantum mechanics the equation of motion is replaced by the operator equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}(t)\Psi\,, \tag{10}$$

where the Hamiltonian $\hat{H}$ is

$$\hat{H}(t) = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 + U(\vec{r}) + e\phi\,, \tag{11}$$

and where $U(\vec{r})$ is the static potential describing the interaction of the elementary charges comprising the system. Despite the explicit appearance of the electromagnetic potentials in Eq. (11), the results of the application of Eqs. (10) and (11) to physical problems are gauge invariant.[8] In particular the gauge transformation defined by Eqs. (8a) and (8b) changes the solutions of Eq. (10) into

$$\Psi' = \Psi \exp\left[+\frac{ie}{\hbar c} f(\vec{r}, t)\right]. \tag{12}$$

Consequently the probability distributions which involve the product $\Psi\Psi^*$ are unaffected by that change. Quantities which are similarly invariant to a gauge transformation are the operator for the kinetic momentum $(-i\hbar\nabla - e\vec{A}/c)$ and the operator with units of energy $(e\phi - i\hbar\partial/\partial t)$. The treatment of observable quantities depending upon the electromagnetic fields such as the shift of the energies of the interacting system and the transition rates induced between stationary states present greater problems. The possible dependence upon gauge inferred from conventional perturbation theory will be discussed in the following section as it defines the direction in which an invariant approach is subsequently developed.

GAUGE TRANSFORMATIONS OF TRANSITION PROBABILITIES

Conventional time-dependent theory

In the conventional time-dependent perturbation theory for the interaction of a charged particle with the electromagnetic field the interaction operator is configured in terms of the potentials

$$V(t) = e\phi - \frac{e}{2mc}(\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) + \frac{e^2}{2mc^2}A^2\,, \tag{13}$$

while the basis set of states are taken to be the eigenfunctions $\Psi_n^{(0)}(\vec{r}, t)$ of the unperturbed Hamiltonian $\hat{H}_0$ describing the particle in field-free space

$$\hat{H}_0 = \frac{\vec{p}^2}{2m} + U(\vec{r})\,, \tag{14}$$

where $\vec{p}$ is the operator $-i\hbar\nabla$. Then

$$\hat{H}_0\Psi_n^{(0)} = i\hbar\frac{\partial \Psi_n^{(0)}}{\partial t} \tag{15}$$

and

$$\Psi_n^{(0)}(\vec{r}, t) = \psi_n^{(0)}(\vec{r})e^{-(i/\hbar)E_n^{(0)}t}\,, \tag{16}$$

where $E_n^{(0)}$ is the energy of the nth basis state and

$$\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}\,. \tag{17}$$

The actual state of the system at some time t is given by the solution to the Schrödinger equation including the interaction

$$i\hbar\frac{\partial \Psi}{\partial t} = (\hat{H}_0 + V(t))\Psi\,. \tag{18}$$

If a transition is conceived to occur from some initial state n_0 of the field-free system $\Psi_{n_0}^{(0)}(\vec{r}, 0)$ to some final state $\Psi_n^{(0)}(\vec{r}, t)$, it is described by the expansion coefficient

$$\alpha_{nn_0}(t) = (\Psi_n^{(0)}, \Psi_{n_0}) \equiv \int \Psi_n^{(0)}(\vec{r}, t)^*\Psi_{n_0}(\vec{r}, t)dq\,, \tag{19}$$

which gives the amplitude of the transition, where $\Psi_{n_0}(\vec{r}, t)$ is a solution of Eq. (18) that describes the state into which the initial state evolves under the influence of the full interaction potential of Eq. (13). Necessarily $\Psi_{n_0}(\vec{r}, 0) = \Psi_{n_0}^{(0)}(\vec{r}, 0)$. Since the transition amplitude is an expansion coefficient, any general solution to Eq. (18), $\Psi_n(\vec{r}, t)$ can be written in terms of the field-free functions

$$\Psi_n(\vec{r}, t) = \sum_m \alpha_{mn}(t)\Psi_m^{(0)}(\vec{r}, t)\,, \tag{20}$$

with the initial conditions being $\alpha_{mn}(0) = \delta_{mn}$. The explicit values of the transition amplitudes can be found from the usual coupled equations

$$i\hbar\frac{d}{dt}\alpha_{mn}=\sum_{m'}V_{mm'}(t)\alpha_{m'n}(t)\,, \tag{21}$$

where the $V_{mm'}(t)$ are the matrix elements

$$(\Psi_m^{(0)}(\vec{r},t)|\,V(t)\,|\Psi_{m'}^{(0)}(\vec{r},t))\,.$$

In another gauge such as the primed gauge defined by Eqs. (8a) and (8b), the possible states of the system satisfying Eq. (18) with $V'(t)$ being given by Eq. (13) written with the primed potentials are the Ψ' of Eq. (12) expressed in terms of the Ψ of Eq. (18) for the original unprimed gauge. However, in the new gauge the field-free solutions at $t=0$ no longer correspond to individual solutions $\Psi_n'(\vec{r},0)$ of the full Hamiltonian, but rather to linear combinations of the $\Psi_n'(\vec{r},0)$, so that the initial state might be expressed as

$$\Psi_{n_0}^{(0)}(\vec{r},0)=\sum_m\gamma_{mn_0}\Psi_m'(\vec{r},0)\,, \tag{22}$$

where the

$$\gamma_{mn_0}=(\Psi_m'(\vec{r},0),\Psi_{n_0}^{(0)}(\vec{r},0))$$
$$=(\Psi_m(\vec{r},0)|e^{-(ie/\hbar c)f(\vec{r},0)}|\psi_{n_0}^{(0)}(\vec{r},0))\,.$$

After a time t this solution becomes

$$\Phi_{n_0}(\vec{r},t)=\sum_m\gamma_{mn_0}\Psi_m'(\vec{r},t)\,, \tag{23}$$

where $\Phi_{n_0}(\vec{r},t)$ is the solution of the full Hamiltonian into which the initial state $\Psi_{n_0}^{(0)}(\vec{r},0)$ evolves as time proceeds. The transition amplitude then becomes by analogy with Eq. (19) $\alpha'_{nn_0}(t)$ $=(\Psi_n^{(0)},\Phi_{n_0})$. Substituting Eq. (23) into this expression together with the value of γ_{nn_0} finally gives

$$\alpha'_{nn_0}(t)=\sum_{l,m}F_{nl}(t)F^*_{n_0m}(0)\alpha_{lm}(t)\,, \tag{24}$$

where

$$F_{mn}(t)=(\Psi_m^{(0)}(\vec{r},t)|e^{(ie/\hbar c)f(\vec{r},t)}|\Psi_n^{(0)}(\vec{r},t))\,.$$

Equation (24) is the basic relation describing the transformation of the transition amplitudes resulting from the change of gauge from the unprimed to the primed potentials shown in Eqs. (8a) and (8b).

Resonant transitions

The gauge invariance of the resonant part of the transition amplitudes defined by Eq. (19) can be shown to follow as a consequence of the transformation Eq. (24). It is assumed for simplicity in this development that the radiation field can be represented as a linear sum of components oscillating at discrete frequencies $\omega_1,\omega_2,\ldots,\omega_N$, and that the function f defining the transformation of the gauge also has components of finite magnitude at the frequencies $\omega_1,\ldots,\omega_N$. However, no loss of generality occurs from this assumption because the derivation is unchanged by the development of the functions as Fourier integrals.

For example, the potentials describing a typical radiation field might be expressed in the radiation gauge as

$$\begin{aligned}&\Phi=0\,,\\&\vec{A}=\vec{A}_1\sin(\omega_1t-\vec{k}_1\cdot\vec{r}+\alpha_1)\\&\quad+\vec{A}_2\sin(\omega_2t-\vec{k}_2\cdot\vec{r}+\alpha_2)+\cdots\,,\end{aligned} \tag{25}$$

where $\vec{A}_1$ and $\vec{A}_2$ are constant vector amplitudes. The gauge of Göppert-Mayer,[1]

$$\begin{aligned}&\Phi'=-\vec{E}_1\cdot\vec{r}\cos(\omega_1t-\vec{k}_1\cdot\vec{r}+\alpha_1)\\&\quad-\vec{E}_2\cdot\vec{r}\cos(\omega_2t-\vec{k}_2\cdot\vec{r}+\alpha_2)+\cdots\,,\\&\vec{A}'\sim0\,,\end{aligned} \tag{26}$$

where $E_n=(\omega_n/c)A_n$ is the electric field intensity of the nth component, is obtained by the transformation of Eqs. (8a) and (8b) defined by the function

$$\begin{aligned}f(\vec{r},t)=&-\vec{A}_1\cdot\vec{r}\sin(\omega_1t-\vec{k}_1\cdot\vec{r}+\alpha_1)\\&-\vec{A}_2\cdot\vec{r}\sin(\omega_2t-\vec{k}_2\cdot\vec{r}+\alpha_2)+\cdots\,.\end{aligned} \tag{27}$$

It is assumed that the interacting system, the atom or molecule which will emit or absorb the radiation, is initially in state n_0 and that only one final state n is resonant with transitions composed of integral numbers of photons of the available frequencies. Further, it is assumed that for only one set of integers $\{n_i,m_i\}$ is Eq. (4) satisfied for the transition from $n_0\to n$ of the lowest order N. Then the time dependence of the resonant part $\alpha^R_{nn_0}(t)$ of the transition amplitude in the original unprimed gauge $\alpha_{nn_0}(t)$ that leads to a probability which grows with time of finding the system in the final state is

$$\alpha^R_{nn_0}(t)=K_N\frac{e^{i(\omega_{nn_0}-\omega_1-\omega_2-\cdots)t}-1}{(\omega_{nn_0}-\omega_1-\omega_2-\cdots)}\,, \tag{28}$$

where N is defined in connection with Eq. (4) as mentioned above, the ω_n can be positive or negative corresponding to the absorption or emission of a photon, respectively, and K_N is a constant composed of matrix elements.

For example, in single-photon transitions, the operator of interaction in Eq. (18) contains terms with time dependence $e^{2i\omega_1t}$, $e^{i\omega_1t}$, $e^{-i\omega_1t}$, and $e^{-2i\omega_1t}$, where ω_1 can be positive or negative and corresponds to the single frequency assumed to describe the electromagnetic potential in a form such as given in Eqs. (25) or (26). In our convention the resonant part $\alpha^R_{nn_0}$ for which $\omega_{nn_0}-\omega_1=0$ results from the potential term with time dependence

$e^{-i\omega_1 t}$ which can be denoted $V_1 e^{-i\omega_1 t}$. Then for this single-photon transition $N=1$, and K in Eq. (28) is found from Eq. (21) to be

$$K_1 = -(V_1)_{nn_0}/\hbar \tag{29a}$$

where $(V_1)_{nn_0} = (\psi_n^{(0)}(\vec{r})|V_1|\psi_{n_0}^{(0)}(\vec{r}))$.

For two-photon transitions $N=2$, and the operator of interaction contains terms with time dependence $e^{\pm 2i\omega_1 t}$, $e^{\pm 2i\omega_2 t}$, $e^{\pm i(\omega_1+\omega_2)t}$, and $e^{\pm i(\omega_1-\omega_2)t}$, where again ω_1 and ω_2 can be positive or negative while describing the absorption or emission, respectively, at the two frequencies of the components of the radiation fields. The terms with a resonant contribution for which $\omega_{nn_0}-\omega_1-\omega_2=0$ in the second order of interaction are $V_1 e^{-i\omega_1 t}$, $V_2 e^{-i\omega_2 t}$, and $V_{12}e^{-i(\omega_1+\omega_2)t}$. The terms V_1 and V_2 are linear in the potentials and their resonant contribution appears in the second-order iteration of the conventional perturbation method for the solution of Eq. (21). The term V_{12} is quadratic in the potentials and arises from the term $(e^2/2mc^2)A^2$, so that its resonant contribution appears in the first-order iteration. Then

$$K_2 = -\frac{(V_{12})_{nn_0}}{\hbar} + \frac{1}{\hbar^2}\sum_{n'}\left[\frac{(V_1)_{nn'}(V_2)_{n'n_0}}{\omega_{n'n_0}-\omega_2} + \frac{(V_2)_{nn'}(V_1)_{n'n_0}}{\omega_{n'n_0}-\omega_1}\right], \tag{29b}$$

where the second of the contributions is the one conventionally used to describe the predominant part of the transition amplitude for a two-photon process.

The term retained in Eq. (28) can be identified as the resonant term because the limit of $|(e^{i(\Delta\omega)t}-1)/\Delta\omega|^2$ is proportional to $t\,\delta(\Delta\omega)$, the Dirac δ function, when $t\to\infty$ and at the frequencies corresponding to the N-order resonance $\{n_i, m_i\}$, $\Delta\omega\to 0$. Other nonresonant terms for which $\Delta\omega \neq 0$ that arise in solving Eq. (21) do not lead to physically observable transitions and have been neglected in Eq. (28).

The time dependence of the primed amplitudes defined by Eq. (24) similarly results from terms showing behavior which is either resonant or nonresonant with the transition frequency ω_{nn_0}. For example, terms such as $F_{nl}(t)F^*_{n_0m}(0)\alpha_{lm}(t)$, when either $l\neq n$ or $m\neq n_0$, depend inversely on the Nth-order frequency differences through the $\alpha^R_{lm}(t)$. If the sum of the N-photon frequencies were $\sum_{i=1}^N \omega_i = \omega$, then the terms containing $\alpha_{lm}(t)$ would include the potentially resonant parts $\alpha^R_{lm}(t)$ $\propto (\omega_{lm}-\omega)^{-1}$ and the resulting product would be resonant when the transition frequency was $\omega = \omega_{lm}$. However, it has been assumed in this development that the transition occurs between n_0 and n so that in this case $\alpha^R_{lm}(t)\propto(\omega_{lm}-\omega_{nn_0})^{-1}$, which cannot be divergent because of the initial assumptions of this section designed to avoid the accidental equality of transition energies between different pairs of levels. Terms of this type are *nonresonant* in their temporal behavior.

The only other type of terms appearing in the transformation Eq. (24) are of the type $F_{nn_0}(t)F^*_{n_0n}(0)\alpha_{n_0n}(t)$ and $F_{nn}(t)F^*_{n_0n_0}(0)\alpha_{nn_0}(t)$. Both appear resonant *a priori* because of the form of the $\alpha^R_{nn_0}(t)$ and $\alpha^R_{n_0n}(t)$ given by Eq. (28). However, in the first the $\alpha^R_{n_0n}(t)$ describes the inverse transition $n\to n_0$ for which $\sum_{i=1}^N \omega_i = \omega_{nn_0} = -\omega_{n_0n}$ so that the denominator becomes $(2\omega_{nn_0})^{-1}$ at "resonance" rather than at zero and only the second of the terms leads to the δ function in the transition probability. Since the F_{ij} are functions of time which are everywhere finite, the transformation equation of the resonant parts leading to transitions at the frequency ω_{nn_0} becomes

$$\alpha'_{nn_0}(t) = F_{nn}(t)F^*_{n_0n_0}(0)\alpha^R_{nn_0}(t) + \text{nonresonant terms}, \tag{30a}$$

or

$$\alpha'_{nn_0}(t) = G(t)K_N\frac{e^{i(\Delta\omega)t}-1}{\Delta\omega} + \text{nonresonant terms}, \tag{30b}$$

where $G(t) = F_{nn}(t)F^*_{n_0n_0}(0)$ and $\Delta\omega = \omega_{nn_0} - \sum_{i=1}^N \omega_i$ which goes to the limit of zero as precise resonance is obtained between the sum of the N-photon energies, respecting the convention on sign which identifies absorption or emission, and the transition energy $\hbar\omega_{nn_0}$.

The transition probabilities then become in the respective gauges

$$w_{n\leftarrow n_0} = |\alpha_{nn_0}|^2 \tag{31a}$$

and

$$w'_{n\leftarrow n_0} = |\alpha'_{nn_0}|^2. \tag{31b}$$

As is generally demonstrated in time-dependent perturbation theory,[9] only the resonant term leads to a transition probability of the form $w\propto t\,\delta(\Delta\omega)$ which corresponds to a physically observable transition to a final stationary state. Thus retaining in the primed gauge only the resonant terms in the transition amplitude that lead to physically meaningful transitions gives the effective transformation equation

$$\alpha'_{nn_0} = F_{nn}(t)F^*_{n_0n_0}(0)\alpha^R_{nn_0}(t). \tag{32}$$

To determine the dependence upon gauge, or the invariance, from Eq. (32) requires consideration of the order of the dependence of the various terms

upon the intensity of the radiation fields. Expanding the phase factors appearing in the matrix elements, F_{nl},

$$e^{(ie/\hbar c)f(\vec{r},t)} = 1 + \frac{ie}{\hbar c} f(\vec{r},t) + \cdots , \tag{33}$$

gives

$$F_{mn}(t) = \delta_{mn} + \frac{ie}{\hbar c} f_{mn}(t) + \cdots , \tag{34}$$

where the matrix elements, $f_{mn}(t)$ $= (\Psi_m^{(0)}(\vec{r},t)|f(\vec{r},t)|\Psi_n^{(0)}(\vec{r},t))$. Since f is generally proportional to either the fields or the potentials of the electromagnetic radition, Eq. (34) represents an expansion in increasing orders of field strength. The α_{ij} are obtained from Eq. (21) through the usual iteration

$$\alpha_{mn}^{(k+1)}(t) = -\frac{1}{\hbar}\int_0^t \sum_{m'} V_{mm'}(t)\alpha_{m'n}^{(k)}(t)dt , \tag{35}$$

with the initial condition $\alpha_{mn}^{(0)}(t) = \delta_{mn}$ and $\alpha_{mn}(t)$ $= \sum_k \alpha_{mn}^{(k)}(t)$. The $V_{mm'}$ are also proportional to the fields or the potentials, either linearly or quadratically, so that the $\alpha_{mn} = \delta_{mn} + \alpha_{mn}^{(1)} + \cdots$ represents an expansion in increasing powers of the field, but it does not necessarily follow that $\alpha^{(k)} \propto A^k$. Since $V_{nn'}$ may contain quadratic powers of the fields, the kth order of iteration will contain powers of A ranging from k to $2k$. It is useful then to evaluate the gauge dependence of the transformation Eq. (35) not in terms of the order of iteration k but in terms of the coefficients of the terms containing comparable orders of dependence on the electromagnetic potentials. Considering only the resonant parts of the transition amplitudes which lead to observable transitions, they can be written in terms of their components proportional to the various powers of the potentials as

$$\alpha_{nn_0}^R = \alpha_{nn_0,N}^R + \alpha_{nn_0,N+1}^R + \cdots , \tag{36}$$

where $\alpha_{nn_0,N}^R$ is that part proportional to A^N. Terms lower than N need not be considered for the N-photon transition modeled here. Any particular term $\alpha_{nn_0,N}^R$ may contain components from orders of iteration varying from $M \geq N/2$ to $M = N$. A similar equation to Eq. (36) can be written for the primed gauge. Then substituting into Eq. (32) together with Eq. (34) gives

$$\alpha_{nn_0,N}'^R(t) + \alpha_{nn_0,N+1}'^R(t) + \cdots = \left(1 + \frac{ie}{\hbar c} f_{nn}(t) + \cdots\right)\left(1 - \frac{ie}{\hbar c} f_{n_0n_0}(0) + \cdots\right)[\alpha_{nn_0,N}^R(t) + \alpha_{nn_0,N+1}^R(t) + \cdots]$$

$$+ \text{nonresonant terms.} \tag{37}$$

As discussed above, the f are at least linearly proportional to the potentials. Equating comparable powers of the electromagnetic potentials gives

$$\alpha_{nn_0,N}'^R(t) = \alpha_{nn_0,N}^R(t) \tag{38}$$

for the lowest order of interaction with the potentials of the field, thus demonstrating the gauge invariance of the lowest-order transition probability describing a resonant N-photon process.

The quantities $\alpha_{nn_0,N}^R(t)$, although superficially less general than the α_{nn_0}, actually represent the transition probabilities as generally understood. An N-photon process requires at least an N-fold dependence upon the radiation intensity and resonance is routinely assumed in the conventional developments of transition probabilities leading to physically observable changes of state. It is remarkable that Eq. (38) demonstrates a general gauge invariance of the transition probability for an N-order electromagnetic transition without assumptions about the type or symmetry of the particular interaction. This is to be contrasted with the most general previous treatment of gauge invariance,[5] in which the invariance of a two-photon process mediated by electric dipole interactions was demonstrated when a change was made between two specific gauges. The proof demonstrated in that work rested upon the completeness of the sums over the intermediate states. This can be understood in the context of the development presented here, since the sum over all nonresonant intermediate $(N-M)$-photon transitions, where $N > M > 0$, gives the transition probability for a resonant N-photon process and it is the resonant nature of the N-order process that ensures the invariance of the transition probability depending upon the Nth power of the intensity. Related results demonstrating the equivalence of the energies of the interactions with external fields described in differing gauges have been reported recently by Goldman[10] for the lowest order of the time-dependent perturbations.

It must be emphasized that the gauge invariance specified by Eq. (38) concerns the entire transition probability describing an N-photon process and includes terms usually neglected as being small. For example, the two-photon amplitude $\alpha_{nn_0,2}^R$ given by Eq. (28) contains in the K_2 factor, not only the sums over single-photon transitions to nonresonant intermediate states, which are the only terms usually retained in two-photon transition probabilities, but also the term $-(V_{12})_{nn_0}/\hbar$ which results from the part of the interaction $(e^2/2mc^2)A^2$ which is usually neglected. Thus the two-photon transition probability, as usually ex-

pressed, is gauge invariant only to within the error introduced by neglecting the A^2 term from the sum in K_2 which is gauge invariant. In specific cases the remainder resulting from neglect of the A^2 term may be separately gauge invariant as shown by Kobe[5] for the specific case of two-photon electric dipole transitions. The general gauge invariance of a resonant, N-photon transition pertains to the entire transition probability describing the dependence of the transition rate upon the Nth power of the radiation intensity.

Gauge-dependent amplitudes—"nonresonant transitions"

Although the amplitudes leading to transitions which are resonant for the absorption of N photons are gauge invariant, individual component transitions to intermediate states involving the nonresonant absorption of $(N-M)$ photons generally are not gauge invariant when $N>M>0$. The gauge-dependent nature of nonresonant single-photon transitions was first recognized in 1978 by Kobe and Smirl,[3] although the lack of physical significance of such a dependence was not mentioned. A similar gauge dependence of nonresonant, two-photon processes was demonstrated subsequently by Kobe,[5] but again without emphasizing that the process cannot lead to a physical result incorporating a gauge dependence.

For example, even in the simpler first-order process the physical meaning of a "nonresonant" transition is questionable. The nonresonant absorption of a single photon by an atom might occur as an intermediate step in a Raman or scattering process.[11] This cannot lead to the creation of a stationary state, and hence the transition becomes physically observable only if another nonresonant step finishes the process. To become physically observable the final state populated by the composite process must have a lifetime comparable to the time τ required for a physical measurement. Then the uncertainty relation for the energy implies an overall resonance to within the accuracy $\hbar/\tau$. Thus the overall process, which is the only one that is physically observable, becomes a resonant and therefore gauge-independent process.

To examine the gauge dependence of the nonresonant transitions to intermediate states of the overall transition resonant with N photons, in the formalism developed in the previous section the general transformation of Eq. (24) can be written explicitly in terms of successive orders k of the iterations of the $\alpha_{nn_0}^{(k)}$ by substituting into Eq. (24) the expansions given in Eq. (33) and (34), and recalling $\alpha_{mn}=\delta_{mn}+\alpha_{mn}^{(1)}+\alpha_{mn}^{(2)}+\cdots$ to obtain

$$\alpha'^{(1)}_{nn_0}(t)+\alpha'^{(2)}_{nn_0}(t)+\cdots=\alpha^{(1)}_{nn_0}(t)+\frac{ie}{\hbar c}[f_{nn_0}(t)-f_{nn_0}(0)]\alpha^{(2)}_{nn_0}(t)+\frac{ie}{\hbar c}\sum_l\,[f_{nl}(t)\alpha^{(1)}_{ln_0}(t)-\alpha^{(1)}_{nl}(t)f_{ln_0}(0)]$$
$$-\frac{e^2}{\hbar^2c^2}\sum_l\,[f_{nl}(t)f_{ln_0}(t)-f_{nl}(t)f_{ln_0}(0)+f_{nl}(0)f_{ln_0}(0)]+\cdots. \tag{39}$$

Each term of a particular order k of iteration contains resonant and nonresonant terms and may depend upon orders of the radiation intensity as great as $2k$. For example, the conventional transition amplitudes at the first order of iteration can be seen to depend upon gauge through the appearance of the term $(ie/\hbar c)[f_{nn_0}(t)-f_{nn_0}(0)]$ which in general is not zero. Expression (39) represents a generalization of the statement of the gauge dependence of nonresonant first-order transition and second-order transitions considered by previous authors.[12]

The fact that a gauge transformation of the amplitudes of the nonresonant, nonphysical transitions to intermediate states introduces terms dependent upon both the gauge of the fields and implicitly upon the basis set of the representation used in the computation of the matrix elements f_{ij} does not present an apparent problem. The computation of the probabilities of a process of sufficiently higher order involving enough photons to be resonant and hence physically observable, will necessarily contain terms describing transitions to the intermediate states whose gauge dependence will be precisely compensating so that the overall invariance of Eq. (38) is maintained. Nevertheless, the concern for maintaining gauge invariance of even the nonphysical intermediate steps has continued to motivate[3] an examination of basis sets in which the nonresonant matrix elements adding to the transformation of the α_{nn_0} might not appear. Unfortunately, certain choices of basis set made according to this criterion tend to exclude some physically meaningful processes, while other possible choices predict that nonzero transition probabilities will occur in the absence of real electromagnetic fields. These problems and the means for avoiding them will be examined in the following sections.

INVARIANT FORMULATIONS

Basis sets

Considerable attention has been given in the literature[3,5,7] to the development of alternative methods to the conventional time-dependent perturbation theory for the computation of transition probabilities by invariant schemes, regardless of the resonant or nonresonant nature of the transition being described. As can be seen from the previous discussion of the conventional method a gauge dependence can result from the fact that according to Eq. (12) the solutions to the Schrödinger equation including the electromagnetic interactions change by a variable phase factor which depends upon the gauge, while the basis set of states described by Eqs. (14) to (17) are, of course, unaffected by the gauge. It is evident that if the initial as well as the final state of the transition were to transform with gauge by the same phase factor, the resulting expansion coefficients and hence the transition amplitudes would not contain the dependence upon the function f determining the gauge of the potentials. Thus the gauge invariance of all of the transition amplitudes would be obtained.

A technique for choosing a basis set of initial states having the desired dependence upon gauge was first suggested by Yang,[7] who included in the Hamiltonian defining the basis states part of the electromagnetic potentials. However, Yang's choice is not unique and appears to have excluded certain physically meaningful situations as will be discussed in the following section. Subsequent authors[3,5] continued the use of the same basis set. A more general representation is developed here from the basis set resulting from the solution of the eigenvalue equation

$$\hat{H}_B\Psi(\vec{r},t)=E(t)\Psi(\vec{r},t) \tag{40}$$

for the basis-defining Hamiltonian

$$\hat{H}_B=\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}-\nabla\lambda\right)^2+U(\vec{r})+\mu(\vec{r},t)\,, \tag{41}$$

where $\lambda(\vec{r},t)$ and $\mu(\vec{r},t)$ are functions not depending upon the gauge of Φ and $\vec{A}$. Since the Hamiltonian contains an explicit dependence upon time through the electromagnetic potentials, the eigenvalue of the energy corresponding to a particular state will also depend upon time as indicated in Eq. (40). Such an energy is not conserved in the strict sense, but rather is an analog to the energy of an adiabatic state that may change with the variation of a parameter included in the Hamiltonian without leading to a change of the state itself.

The solutions of Eq. (40) transform with changes of gauge according to Eq. (12). Since λ and μ are completely arbitrary, the requirement of gauge invariance does not uniquely determine the nature of the basis set, contrary to the implicit assumption of Yang. Yang,[7] as well as subsequent authors,[3,5] exclusively employed a basis set equivalent to the solutions of Eq. (40) for $\lambda=0$ and $\mu=0$.

From the more general representation of Eq. (41) it will be shown that the use of the class of basis sets obtained from the assumption that $\lambda=0$ for an arbitrary $\mu(\vec{r},t)$ is equivalent to the development of the conventional time-dependent perturbation theory. Both predict the same amplitudes for the resonant transitions. All members of the class result in transition amplitudes which are invariant with respect to changes of gauge, although they are not necessarily equal for the nonresonant transitions.

The term in the $\hat{H}_B$ Hamiltonian $\mu(\vec{r},t)$ appears in the form of a potential energy of the interaction of the charge with the external field. To emphasize this fact it can be expressed $\mu=e\phi_0(\vec{r},t)$, where $\phi_0(\vec{r},t)$ is an arbitrary potential written in terms of the fields and thus is not dependent upon the gauge of the potentials. For the $\lambda=0$ class of basis sets, the equations from which the transition amplitudes are developed in this invariant scheme include the expression for the Hamiltonian defining the basis sets describing the initial and final states

$$\hat{H}_B=\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2+U(r)+e\phi_0\,, \tag{42a}$$

the eigenvalue equation for these states

$$\hat{H}_B\Psi_n(\vec{r},t)=E_n(t)\Psi_n(\vec{r},t)\,, \tag{42b}$$

the full Hamiltonian of the interaction with the electromagnetic fields

$$\hat{H}(t)=\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2+U(r)+e\phi\,, \tag{43a}$$

where ϕ is the real electromagnetic scalar potential, and the Schrödinger equation

$$\hat{H}(t)\Psi=i\hbar\frac{\partial\Psi}{\partial t}\,. \tag{43b}$$

It should be reemphasized that changes of gauge of the potentials $\Phi,\vec{A}$ transform both the basis sets satisfying Eq. (42b) and the solutions of Eq. (43b) according to Eq. (12), while the energy eigenvalues of Eq. (42b) remain invariant, $E_n'(t)=E_n(t)$.

It is most convenient to develop the solutions to Eqs. (42a), (42b), (43a), and (43b) in a gauge[13] for which $\phi=\phi_0$, so that $\hat{H}(t)=\hat{H}_B$. Since the transition amplitudes are invariant to this, as well as other gauge changes, generality is maintained. However, in addition to facilitating computation this particular choice is more comfortable from a physical viewpoint. The basis set describing the initial and final states of the system is preserved in an adia-

batic sense during the time the perturbation acts to cause the transition. Physically, the electromagnetic transition can be perceived as occurring in two steps. First, as the fields develop the system undergoes an adiabatic passage, without transitions, from one of the field-free states satisfying Eq. (15) to one of the basis states satisfying Eq. (42b) for $\phi_0 = \phi$ as suggested by the Ehrenfest theorem.[14] Subsequently, the same time-dependent interactions are viewed as causing transitions from pure states of the basis set, which continues to be a basis set throughout the process. The transitions produce linear superpositions of the basis states with time-varying amplitudes that are interpreted as the transition probabilities, since the basis states ultimately reverse the adiabatic passage to become again field-free states as the electromagnetic interaction terminates.

Perturbation method

Quantitatively the process of transition is described in the $\phi = \phi_0$ gauge by expanding[15] the solutions of Eqs. (43a) and (43b) assuming nondegenerate base states as

$$\Psi(\vec{r},t) = \sum_n C_n(t)\Psi_n(\vec{r},t)e^{-(i/\hbar)E_n^{(0)}t}. \tag{44}$$

Substituting into Eq. (43b) gives

$$i\hbar\frac{dC_n}{dt} = C_n(E_n(t) - E_n^{(0)}) - i\hbar\sum_{n'} e^{i\omega_{nn'}t}C_{n'}\int \Psi_n^*\frac{\partial\Psi_{n'}}{\partial t}\,dq, \tag{45}$$

where $\omega_{ij} = (E_i^{(0)} - E_j^{(0)})/\hbar$, and where $E_n^{(0)}$ is the initial eigenvalue of the energy of the nth state. At the time $t = 0$ the system is assumed to be in the initial state n_0, so that $C_n(0) = \delta_{nn_0}$ and the $C_n(t)$ represent the amplitudes of the transitions from $n_0 \to n$ in this invariant method of development. For this approach Eq. (45) corresponds to Eq. (21) of the conventional method.

The solution of the coupled set of equations represented by Eq. (45) requires the substitution of expressions for the basis functions $\Psi_n(\vec{r},t)$ and these may be obtained by the conventional time-independent perturbation scheme of iteration for which $\hat{H}_B = \hat{H}_0 + V(t)$ and the time is treated as a parameter. The expansions

$$\Psi_n(\vec{r},t) = \psi_n^{(0)}(\vec{r}) + \Psi_n^{(1)}(\vec{r},t) + \Psi_n^{(2)}(\vec{r},t) + \cdots, \tag{46a}$$

$$E_n(t) = E_n^{(0)} + E_n^{(1)}(t) + E_n^{(2)}(t) + \cdots, \tag{46b}$$

$$C_n(t) = \delta_{nn_0} + C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots, \tag{46c}$$

where the superscript indicates the order of iteration and not necessarily the order of the dependence on the fields when substituted into Eq. (45), and the resulting terms equated according to the various orders of iteration give through second order, for $n \neq n_0$,

$$C_n^{(0)} = \delta_{nn_0}, \tag{47a}$$

$$i\hbar\frac{d}{dt}C_n^{(1)} = i\hbar e^{i\omega_{nn_0}t}\frac{(\partial V_{nn_0}/\partial t)}{E_n^{(0)} - E_{n_0}^{(0)}}, \tag{47b}$$

$$i\hbar\frac{d}{dt}C_n^{(2)} = -i\hbar e^{i\omega_{nn_0}t}\left[\sum_k{}' \frac{\partial(V_{nk}V_{kn_0})/\partial t}{(E_{n_0}^{(0)} - E_k^{(0)})(E_{n_0}^{(0)} - E_n^{(0)})} - \frac{\partial(V_{n_0n_0}V_{nn_0})/\partial t}{(E_{n_0}^{(0)} - E_n^{(0)})^2}\right] - i\hbar e^{i\omega_{nn_0}t}\sum_k{}' \frac{V_{kn}^*(\partial V_{kn_0}/\partial t)}{(E_n^{(0)} - E_k^{(0)})(E_{n_0}^{(0)} - E_k^{(0)})} - i\hbar\sum_{n'}{}' e^{i\omega_{nn'}t}\frac{(\partial V_{nn'}/\partial t)}{E_{n'}^{(0)} - E_n^{(0)}}C_{n'}^{(1)} + C_n^{(1)}V_{nn}, \tag{47c}$$

and for n_0,

$$i\hbar\frac{d}{dt}C_{n_0}^{(1)} = V_{n_0n_0}, \tag{47d}$$

where $V_{mn} = \int\psi_m^{*(0)}(\vec{r})V(t)\psi_n^{(0)}(\vec{r})dq$, $E_n(t) = E_n^{(0)} + V_{nn}$, and the convention regarding the primed summation is that particular indices leading to zeros in the denominators are excluded from the sum. In second order $C_{n_0}^{(2)} = 0$ and does not appear in the above equations. Specific examples for one-photon and two-photon absorptions are developed in the following sections and considerable simplification is found.

Single-photon processes

The part of the interaction operator leading to single-photon transitions is of the form $V(t) = V_1e^{-i\omega_1t}$. As in the conventional approach of the preceding sections, ω_1 can be positive or negative to denote the absorp-

tion or the emission of a photon, respectively. Substituting this form of the potential into Eq. (47b) and retaining only the resonant contributions to $C_n^{(1)}$ gives

$$C_n^{(1)} = -i\frac{\omega_1}{E_n^{(0)} - E_{n_0}^{(0)}}(V_1)_{nn_0}\int_0^t e^{i(\omega_{nn_0}-\omega_1)t'}\,dt'. \tag{48}$$

Then the corresponding transition probability becomes

$$w_{n\leftarrow n_0} = \frac{1}{\hbar^2}|(V_1)_{nn_0}|^2\left|\int_0^t e^{i(\omega_{nn_0}-\omega_1)t'}dt'\right|^2. \tag{49}$$

Two-photon processes

As mentioned in the development leading to Eq. (29b) describing the transition amplitude in the conventional application of time-dependent perturbation theory, the important components of the potential for two-photon processes are $V(t) = V_1 e^{-i\omega_1 t} + V_2 e^{-i\omega_2 t} + V_{12}e^{-i(\omega_1+\omega_2)t}$. Substituting this expression into Eq. (47b), Eq. (47c), and Eq. (47d) and retaining only the resonant terms for the simultaneous interaction with one photon of each frequency gives

$$i\hbar\frac{d}{dt}C_n^{(1)} = \frac{\hbar(\omega_1+\omega_2)}{E_n^{(0)} - E_{n_0}^{(0)}}(V_{12})_{nn_0}e^{i(\omega_{nn_0}-\omega_1-\omega_2)t} \tag{50a}$$

and

$$\begin{aligned}
i\hbar\frac{d}{dt}C_n^{(2)} = {} & \left[-\frac{\hbar(\omega_1+\omega_2)}{E_n^{(0)} - E_{n_0}^{(0)}}\sum_k{}' \frac{(V_1)_{nk}(V_2)_{kn_0} + (V_2)_{nk}(V_1)_{kn_0}}{E_k^{(0)} - E_{n_0}^{(0)}} + \sum_k{}' \frac{\hbar\omega_2(V_1)_{nk}(V_2)_{kn_0} + \hbar\omega_1(V_2)_{nk}(V_1)_{kn_0}}{(E_n^{(0)} - E_k^{(0)})(E_k^{(0)} - E_{n_0}^{(0)})}\right] e^{i(\omega_{nn_0}-\omega_1-\omega_2)t} \\
& - i\hbar\omega_1\omega_2\sum_k{}' \frac{(V_1)_{nk}(V_2)_{kn_0}}{(E_n^{(0)} - E_k^{(0)})(E_k^{(0)} - E_{n_0}^{(0)})} e^{i(\omega_{nk}-\omega_1)t}\int_0^t e^{i(\omega_{kn_0}-\omega_2)t'}\,dt' \\
& - i\hbar\omega_1\omega_2\sum_k{}' \frac{(V_2)_{nk}(V_1)_{kn_0}}{(E_n^{(0)} - E_k^{(0)})(E_k^{(0)} - E_{n_0}^{(0)})} e^{i(\omega_{nk}-\omega_2)t}\int_0^t e^{i(\omega_{kn_0}-\omega_1)t'}\,dt' \\
& - \frac{i}{E_n^{(0)} - E_{n_0}^{(0)}}\left[\omega_2(V_1)_{nn}(V_2)_{nn_0}e^{-i\omega_1 t}\int_0^t e^{i(\omega_{nn_0}-\omega_2)t'}dt' + \omega_1(V_2)_{nn}(V_1)_{nn_0}e^{-i\omega_2 t}\int_0^t e^{i(\omega_{nn_0}-\omega_1)t'}\,dt'\right] \\
& + \frac{1}{E_n^{(0)} - E_{n_0}^{(0)}}\left[\frac{\omega_2}{\omega_1}(V_1)_{n_0n_0}(V_2)_{nn_0} + \frac{\omega_1}{\omega_2}(V_2)_{n_0n_0}(V_1)_{nn_0}\right] e^{i(\omega_{nn_0}-\omega_1-\omega_2)t} \\
& + \frac{\hbar(\omega_1+\omega_2)}{(E_n^{(0)} - E_{n_0}^{(0)})^2}[(V_1)_{n_0n_0}(V_2)_{nn_0} + (V_2)_{n_0n_0}(V_1)_{nn_0}]e^{i(\omega_{nn_0}-\omega_1-\omega_2)t}.
\end{aligned} \tag{50b}$$

The first-order interaction of Eq. (50a) evidently describes the generation or absorption of sum and difference frequency radiation. Being first order it concerns single photons, but is resonant at the frequency $\pm\omega_{nn_0} = |\omega_1| \pm |\omega_2|$. The second-order interaction of Eq. (50b) relates to the processes more customarily understood to be two-photon transitions: two-photon absorption and emission, Raman scattering, and conventional scattering. It is interesting to observe that the matrix elements are general and may represent radiative interactions of an arbitrary multipolarity.

CONCLUSIONS

Equivalence of the conventional and invariant methods applied to resonant transitions

For single-photon transitions the resonance condition is $E_n^{(0)} - E_{n_0}^{(0)} \to \hbar\omega_1$ and Eq. (48) can be integrated to give

$$C_n^{(1)} = -\frac{(V_1)_{nn_0}}{\hbar}\frac{e^{i(\omega_{nn_0}-\omega_1)t} - 1}{\omega_{nn_0} - \omega_1}, \tag{51}$$

which is identical to the transition amplitude of Eqs. (28) and (29a) obtained by the conventional perturbation method.

For the transitions resonant with the energies of two photons $\omega_{nn_0}-\omega_1-\omega_2\to 0$,

$$C_n^{(1)}=-\frac{(V_{12})_{nn_0}}{\hbar}\,\frac{e^{i(\omega_{nn_0}-\omega_1-\omega_2)t}-1}{(\omega_{nn_0}-\omega_1-\omega_2)}\ , \tag{52a}$$

and for the second-order process

$$\begin{aligned}i\hbar\frac{d}{dt}C_n^{(2)}=\Bigg\{&\sum_{n'}{}'\left[-\frac{1}{E_{n'}^{(0)}-E_{n_0}^{(0)}}+\frac{\hbar\omega_2}{(E_n^{(0)}-E_{n'}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)})}-\frac{\hbar^2\omega_1\omega_2}{(E_n^{(0)}-E_{n'}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)}-\hbar\omega_2)}\right]\\&\times(V_1)_{nn'}(V_2)_{n'n_0}\\&+\sum_{n'}{}'\left[-\frac{1}{E_{n'}^{(0)}-E_{n_0}^{(0)}}+\frac{\hbar\omega_1}{(E_n^{(0)}-E_{n'}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)})}-\frac{\hbar^2\omega_1\omega_2}{(E_n^{(0)}-E_{n'}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)}-\hbar\omega_1)}\right]\\&\times(V_2)_{nn'}(V_1)_{n'n_0}\\&-\sum_{n'=n,\,n_0}\left[\frac{(V_1)_{nn'}(V_2)_{n'n_0}}{\hbar(\omega_{n'n_0}-\omega_2)}+\frac{(V_2)_{nn'}(V_1)_{n'n_0}}{\hbar(\omega_{n'n_0}-\omega_1)}\right]\Bigg\}e^{i(\omega_{nn_0}-\omega_1-\omega_2)t}\ .\end{aligned} \tag{52b}$$

The latter can be simplified considerably by the identity

$$\begin{aligned}-\frac{1}{E_{n'}^{(0)}-E_{n_0}^{(0)}-\hbar\omega_2}=&-\frac{1}{(E_{n'}^{(0)}-E_{n_0}^{(0)})}+\frac{\hbar\omega_2}{(E_n^{(0)}-E_{n'}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)})}\\&-\frac{\hbar^2\omega_1\omega_2}{(E_n^{(0)}-E_{n'}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)})(E_{n'}^{(0)}-E_{n_0}^{(0)}-\hbar\omega_2)}\ ,\end{aligned} \tag{53}$$

and by the analogous relation through interchange of ω_1 and ω_2 to obtain

$$C_n^{(2)}=\sum_{n'}\left[\frac{(V_1)_{nn'}(V_2)_{n'n_0}}{\hbar(\omega_{n'n_0}-\omega_2)}+\frac{(V_2)_{nn'}(V_1)_{n'n_0}}{\hbar(\omega_{n'n_0}-\omega_1)}\right]\frac{e^{i(\omega_{nn_0}-\omega_1-\omega_2)t}-1}{\hbar(\omega_{nn_0}-\omega_1-\omega_2)}\ . \tag{54}$$

This result is identical to that obtained by conventional perturbation theory and presented in Eq. (29b). Since the coefficient of the time-dependent part shown in Eq. (29b) is from the sum $C_n^{(1)}+C_n^{(2)}$, it can be seen that the two approaches yield the same second-order transition amplitudes and, therefore, complete equivalence is obtained between the invariant and conventional formulations.

Comparison of invariant schemes

It was discussed earlier that the requirement for the invariance of the transition amplitudes does not uniquely define a basis set with which calculations may be performed. In fact, any set of states obtained as solutions of the basis-defining Hamiltonian Eq. (41) will lead to the generation of amplitudes for resonant transitions between basis states which are invariant to changes of gauge of the electromagnetic interactions mediating the transition. Since the Hamiltonian $\hat{H}_B$ defining the bases contains completely arbitrary functions entering in the form of electromagnetic forces, infinitely many gauge-invariant schemes may be developed. However, results obtained through the use of different basis sets, while giving equivalent probabilities for resonant transition, do not yield the same results for the general transition amplitudes. The manner in which these amplitudes transform with changes of the basis set will be developed by assuming that the real potentials $\phi,\vec{A}$ are altered by a gauge transformation so that they correspond to the arbitrary potentials ϕ_0 and $\vec{A}_0$ defining the basis.

In particular if it is desired to compare the effects on the transition amplitudes of changing from the basis set defined by ϕ_0 to the set ϕ_0', it is useful to define the function f_0 so that

$$\phi_0'=\phi_0-\frac{1}{c}\,\frac{\partial f_0}{\partial t}\ . \tag{55}$$

Then the $\vec{A}_0'$ and $\vec{A}_0$ are assumed to be the vector potentials corresponding to the ϕ_0' and ϕ_0 in order to completely specify the fields used to define the basis sets through Eq. (42a). The $\vec{A}_0'$ and $\vec{A}_0$ are related by

$$\vec{A}_0'=\vec{A}_0+\nabla f_0\ . \tag{56}$$

That these gauge transformations of the potentials defining the bases do not lead to invariant results, while transformations of the physical fields by Eq. (8a) and (8b) do preserve the invariance can be illustrated by the behavior of the transition amplitudes for the one-photon process given in Eq. (47b).

In the primed basis set defined by Eq. (55), the

$C_n'^{(1)}$ are solutions to the equation analogous to Eq. (47b) obtained by substituting the expressions of Eqs. (55) and (56) for $\phi_0', \vec{A}_0'$ into the interaction operator of Eq. (13) from which the V_{ij} matrix elements needed in Eq. (47b) were obtained. The expression becomes with the simplification of neglecting second-order terms

$$C_n'^{(1)}(t) = C_n^{(1)}(t) - \frac{e}{c}\frac{1}{E_n^{(0)} - E_{n_0}^{(0)}}\left(\Psi_n^{(0)}(\vec{r}, t)\left|\frac{\partial f_0(t)}{\partial t}\right|\Psi_{n_0}^{(0)}(\vec{r}, t)\right)\Big|_0^t . \tag{57}$$

The gauge dependence arises from the second term which is generally nonzero.

Physical choice of the gauge

Since Eq. (57) showed the transition probabilities to be dependent upon the base sets, it is of reasonable concern to inquire which of the possible representations leads to a more physically meaningful result. The idea of the adiabatic passage from the field-free states to those representing instantaneous solutions of the eigenvalue equation for the energies of the system in the external fields is consistent with the nonrelativistic approach used in this work. The time of retardation R/c is small compared to the period $2\pi/\omega$ of the radiation, and the neglect of inductive terms seems justified at least in the dipole approximation. Considering the fields as uniform in the region of the interacting atom suggests the appropriateness of the potential

$$e\phi_0 = -e\vec{E}\cdot\vec{r} - \vec{\mu}\cdot\vec{B} \tag{58}$$

in the definition of a basis set. Such a basis set naturally provides for the adiabatic development of the Stark and Zeeman splittings of the levels of the basis set. Transition amplitudes calculated according to the methods introduced in this work can then represent transitions induced between the states actually occurring in the external fields.

The only other basis sets employed in past computations[3,5,7] of transition probabilities developed according to invariant schemes have been those defined by the potential $\phi_0 = 0$. It would appear that such a choice would preclude adiabatic passage to states shifted by the electric part of the field. For example, if the magnetic field were $\vec{B} = 0$, the electric field could be represented by the time-dependent vector potential $\vec{E} = -(1/c)(\partial\vec{A}/\partial t)$ and $\phi = 0$. This, however, does not affect the energy eigenvalues of the basis set of Eq. (42) while in fact Stark shifts are a physical reality.

While the development of transition amplitudes in a manner invariant to the gauge of the electromagnetic field is philosophically satisfying, to do so introduced nearly equivalent problems of the representation of the basis set of states which must describe the end points of the transition. Gauge dependence is transformed into a representational dependence. Since it appears evident that a physically meaningful transition mediated by electromagnetic fields will be resonant in an adequately high order of development, the problems associated with the gauge dependence of nonresonant processes seem to be artifices resulting from the consideration of an insufficient number of photons in the transition.

It has been shown in this work that a transition which exhibits an overall resonance with some combination of sums and differences of integral numbers of photons of the fields is invariant at the lowest order of the potentials needed to induce the transition. This general result is valid, even when the relatively unsophisticated techniques of the conventional perturbation theory are used. Moreover, since the accidentally poor convergence of the perturbation schemes in the cases of certain potential gauges can be avoided by the use of the physically realistic fields, a highly attractive approach to the computation of multiphoton transition probabilities appears to be the original method of Göppert-Mayer,[1] extended appropriately to accommodate N photons. In the context of the present work it can be seen that that method which involves the minimum complexity would yield highly convergent, gauge-invariant results. At the next level of complexity the invariant scheme introduced in this work, when developed in a basis set generated by the realistic potentials of the problem, would add the possibility for accommodating the adiabatic passage of the system to initial and final states of the transition more nearly characteristic of the physical states involved.

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[10]T. Goldman, Phys. Rev. D 15, 1063 (1977).
[11]W. Heitler, *The Quantum Theory of Radiation*, 3rd ed. (Clarendon, Oxford, 1954), p. 189.
[12]The work of Refs. 3 and 5 concerned only the dependence of the parts of the transition amplitudes equivalent to the $\alpha^R_{nn_0}$ in the terminology of this work.
[13]The gauge transformation accomplishing this change according to Eq. (8a) is generated by the function $f(\vec{r},t)=\int_0^t c(\phi-\phi_0)dt'$.
[14]V. F. Weisskopf, in *Lectures in Theoretical Physics*, edited by W. E. Brittin *et al.* (Interscience, New York, 1961), p. 63.
[15]In the invariant development of this section the expansion coefficients denoted by $C_n(t)$ describe the transition amplitudes and thus play the role of the α_{nn_0} used in the conventional development of the time-dependent perturbation theory described in the previous sections.