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Gauge invariance in non-relativistic electrodynamics

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A novel Hamiltonian scheme for non-relativistic quantum electrodynamics in which the gauge arbitrariness of the field potential is kept explicit is used to study the gauge-dependence properties of various versions of perturbation theory when resonance and line-broadening effects are admitted. Time-dependent perturbation theory is shown to have severe gauge-dependence problems unless ad hoc modifications are made. A time-independent formulation of S-matrix theory is then studied. Far from resonance, the S-matrix is gauge invariant in all orders of perturbation theory due to a very precise cancellation of gauge-dependent terms which requires, among other things, complete sets of intermediate states; energy conservation also has a crucial role. However, an obvious separation of the S-matrix into a resonant (pole) and non-resonant background leads to incomplete cancellation of the gauge-dependent terms. The introduction of the Heitler damping matrix into an integral equation for the T-matrix leads to a gauge-invariant result. This provides the basis for a gauge invariant S-matrix theory of atoms and molecules interacting with electromagnetic radiation that encompasses resonance and damping effects.

Keywords: molecules; resonance; gauge invariance; photons; S-matrix

1. Introduction

Quantum electrodynamics (QED), the covariant quantum theory of electrons and photons, has long been established. The S-matrix, calculated via the Feynman rules, is the main object of the theory inasmuch as, after renormalization, physical questions are answered in terms of appropriate S-matrix elements. The gauge invariance of the S-matrix is easily shown using the equation of continuity within the Lorentz invariant formalism; a variety of gauges for the field potential can then be used, as determined by calculational convenience (Weinberg 1995).

By contrast, the non-relativistic electrodynamics of atoms and molecules has become a much more diverse body of theory with many different types of calculational technique in use depending upon the particular atomic/molecular process of interest. The very first formulation of quantum electrodynamics was Dirac's (1927) quantum mechanical account of an atom interacting with the electromagnetic field, treated as a closed system, and this approach has been developed considerably (Woolley 1975; Loudon 1983; Cohen-Tannoudji *et al.* 1989). Quantization of the field, however, is not always imposed; the semi-classical radiation model in which the atom is quantized, but the field is treated as an external time-dependent classical perturbation, has a long tradition (Pauling & Wilson 1935; Eyring *et al.* 1944; Buckingham 1967) and is still widely used for e.g. molecular light scattering problems (Barron 1982). The semi-classical model is also of considerable current interest because of the easy availability of intense radiation sources for spectroscopic and related experiments; these may be studied computationally by numerical integration of the time-dependent Schrödinger equation for an atom in the presence of a classical field (Moccia *et al.* 1997; Véniard *et al.* 1998).

The question of gauge invariance in the non-relativistic theory in a general sense, which is the concern of this paper, has hardly been dealt with. A wholly conventional calculation in non-relativistic quantum electrodynamics has no possibility of exploring the full consequences of gauge freedom because it starts with a Hamiltonian based on a specific choice of gauge; in practice, either the Coulomb gauge or the multipole gauge. A novel Hamiltonian scheme, summarized briefly in § 2, that retains explicitly the gauge arbitrariness has been proposed recently (Woolley 1996, 1999; see also Babiker & Loudon 1983), and this invites consideration of how it can be used to calculate gauge-invariant quantities using the techniques of non-relativistic quantum mechanics. The present writer has used this general Hamiltonian to show that the S-matrix for non-resonant scattering, which on the energy-shell determines (non-resonant) light scattering cross-sections, is gauge invariant in all orders of perturbation theory (Woolley 1998). It is very desirable that this result (§ 3) be extended to cases where resonance and line broadening are important. A typical example is resonant Raman scattering, which has been well-known in the visible region of the spectrum for many years; with the availability of intense, tunable and polarized X-ray radiation from synchrotron sources, interest in recent years has extended to inelastic X-ray scattering from atoms, molecules and solid surface adsorbates for which numerical simulations based on quantum chemistry techniques are now possible (Luo *et al.* 1994; Triguero *et al.* 1999). These simulations are based on the Kramers–Heisenberg formula modified by damping terms in the Wigner–Weisskopf approximation (Weisskopf & Wigner 1930; Sakurai 1967). Another example is the use of femtosecond lasers for the direct observation of the dynamics of short-lived states (Blake 1990; Sundstrøm 1998), which requires the time evolution of states in the presence of radiation. We do not aim to discuss gauge invariance for any specific calculation, however; rather the concern is to see what can be decided about methods in general.

In this paper we use the general Hamiltonian with both time-dependent and time-independent theoretical methods that have been used to describe radiation phenomena in which damping and line broadening are important physical components, and focus on an explicit requirement for the gauge invariance of physical quantities. In § 4, a formal solution of the time-dependent Schrödinger equation due originally to Heitler (1954), which is based on resolvent theory, is shown to have severe gauge-dependence problems unless ad hoc modifications are made. This means that the theory is unsatisfactory for a fundamental account of time evolution and near resonant phenomena such as the frequency dependence of spectral lineshapes and line broadening, resonance fluorescence and scattering, etc.—its main field of application (Heitler 1954; Power & Zienau 1959; Hameka 1965; Landau & Lifshitz 1971; Blake 1990). In § 5, we return to time-independent methods and show that a straightforward separation of the S-matrix into a resonant (pole) term and a non-resonant background term, as for example is often done with the Kramers–Heisenberg formula, prevents the perfect cancellation of gauge-dependent terms that occurs in the non-resonant case, and also leads to a gauge-dependent result. This difficulty can be avoided, however, by introducing the Heitler damping matrix into an integral equation for the T-matrix (Goldberger 1951). This provides the basis for a gauge-invariant S-matrix theory of atoms and molecules interacting with electromagnetic radiation that encompasses resonance effects. The paper ends (§ 6) with a short discussion.

2. The general Hamiltonian

Non-relativistic electrodynamics is almost invariably based on a Hamiltonian formalism with the Schrödinger equation giving the time evolution of the states. Irrespective of whether or not the field is quantized, there have been traditionally only two formulations (Heitler 1954; Power 1964; Barron 1982; Loudon 1983; Cohen-Tannoudji *et al*. 1989); these are, firstly the Coulomb gauge theory with interaction Hamiltonian,

$$H_{\text{int}} = -\sum_i \frac{e_i}{m_i}\boldsymbol{p}_i \cdot \boldsymbol{A}(\boldsymbol{x}_i) + \sum_i \frac{{e_i}^2}{2m_i}\boldsymbol{A}(\boldsymbol{x}_i)\cdot\boldsymbol{A}(\boldsymbol{x}_i), \tag{2.1}$$

and subsidiary condition,

$$\nabla\cdot\boldsymbol{A}(\boldsymbol{x}) = 0, \tag{2.2}$$

for the field potential, and secondly the multipole Hamiltonian theory in which the interaction is expressed in terms of atomic multipoles and transverse field variables,

$$H_{\text{int}} = -\boldsymbol{d}\cdot\boldsymbol{E}^{\perp} - \boldsymbol{m}\cdot\boldsymbol{B} - \boldsymbol{Q}\cdot\nabla\boldsymbol{E}^{\perp} - \cdots . \tag{2.3}$$

There are examples in the literature of low-order perturbation theory calculations where both interaction Hamiltonians give identical results, e.g. for cross-sections of light scattering processes (Power 1964; Healy 1977). This is not an automatic result, however, and there are also examples of calculations that yield different answers, e.g. for spectral lineshapes (Power & Zienau 1959; Fried 1973).

Although equation (2.3) was originally characterized as providing 'a gauge-invariant Hamiltonian', in contrast to (2.1) (Power & Zienau 1959), we now know that both simply correspond to the choice of different gauges for the field potential (Woolley 1975, 1996, 1999), so the issue of gauge invariance is not removed by changing from (2.1) to (2.3). The transverse field, $\boldsymbol{E}(\boldsymbol{x})^{\perp}$, in (2.3) is the conjugate of the field potential, $\boldsymbol{A}(\boldsymbol{x})$, in the Coulomb gauge, satisfying the commutation relation,

$$[\boldsymbol{A}(\boldsymbol{x})^p, \boldsymbol{E}(\boldsymbol{x}')^{\perp s}] = -\frac{\mathrm{i}\hbar}{\varepsilon_0}\delta^{\perp}(\boldsymbol{x}-\boldsymbol{x}')_{rs}, \tag{2.4}$$

which is specific to this gauge. The full Hamiltonian for charges and electromagnetic radiation is

$$H = H_{\text{c}} + H_{\text{rad}} + H_{\text{int}} \tag{2.5}$$

with

$$H_{\text{c}} = \sum_i \frac{p_i^2}{2m_i} + \sum_{i,j}\frac{e_i e_j}{4\pi\varepsilon_0|\boldsymbol{x}_i - \boldsymbol{x}_j|}, \tag{2.6}$$

$$H_{\text{rad}} = \tfrac{1}{2}\varepsilon_0\int \mathrm{d}^3\boldsymbol{x}\,(\boldsymbol{E}(\boldsymbol{x})^{\perp}\cdot\boldsymbol{E}(\boldsymbol{x})^{\perp} + c^2\boldsymbol{B}(\boldsymbol{x})\cdot\boldsymbol{B}(\boldsymbol{x})), \tag{2.7}$$

the usual Hamiltonians for charged particles with purely electrostatic interactions, and free radiation; equations (2.1) and (2.3) show possible forms for H_{int}.

The relationship between these two formulations is expressed by the Power–Zienau–Woolley (PZW) transformation (Woolley 1971; Babiker *et al.* 1973, 1974; Loudon 1983; Cohen-Tannoudji *et al.* 1989). The PZW transformation results from the action of an operator $\varLambda$ on the full Hamiltonian,

$$\varLambda = \exp\left(\frac{\mathrm{i}}{\hbar} A[\boldsymbol{P}]\right), \qquad A[\boldsymbol{P}] = \int \mathrm{d}^3\boldsymbol{x}\, \boldsymbol{P}(\boldsymbol{x}) \cdot \boldsymbol{A}(\boldsymbol{x}), \tag{2.8}$$

with the Coulomb gauge condition (2.2) for the vector potential $\boldsymbol{A}(\boldsymbol{x})$, and so

$$\mathcal{H} = \varLambda^{-1} H \varLambda = H + \frac{\mathrm{i}}{\hbar}[H, A] + \frac{1}{2!}\left(\frac{\mathrm{i}}{\hbar}\right)^2 [[H, A], A]. \tag{2.9}$$

The vector field $\boldsymbol{P}(\boldsymbol{x})$ in (2.8) satisfies the equation

$$\nabla \cdot \boldsymbol{P}(\boldsymbol{x}) = -\rho(\boldsymbol{x}), \tag{2.10}$$

where $\rho(\boldsymbol{x})$ is the usual charge density; $\boldsymbol{P}(\boldsymbol{x})$ has customarily been referred to as the 'electric polarization field' because of the role of this equation in classical dielectric theory (Lorentz 1916). In the original formulation (Power & Zienau 1959), $\boldsymbol{P}(\boldsymbol{x})$ was written in terms of a multipole series development,

$$\boldsymbol{P}(\boldsymbol{x}) = (\boldsymbol{d} + \boldsymbol{Q} \cdot \nabla + \cdots)\delta^3(\boldsymbol{x}), \tag{2.11}$$

clearly reflecting a prior conception of an 'atom' as a bound collection of charges centred on the origin. Subsequently, it was shown that the multipoles in (2.11) are the leading terms in an expansion of an integral representation for $\boldsymbol{P}(\boldsymbol{x})$ (Fiutak 1963; Woolley 1971),

$$\boldsymbol{P}(\boldsymbol{x}) = \sum_i e_i \int_{C_i}^{\boldsymbol{x}_i} \mathrm{d}\boldsymbol{z}\, \delta^3(\boldsymbol{z} - \boldsymbol{x}), \tag{2.12}$$

where the path C_i is a straight line between the charge at $\boldsymbol{x}_i$ and the origin about which the multipole expansion is made. There is no physical requirement, however, for the lower endpoint of the integration path to be at the 'centre' of a charge distribution; the integration paths can be chosen in any way provided the integral (2.8) with (2.12) exists.

It has recently been shown that an extension of the PZW transformation theory yields a general Hamiltonian for charges interacting with the electromagnetic field in which the gauge of the vector potential need not be specified explicitly (Woolley 1996, 1999). A completely general form for $A[\boldsymbol{P}]$ can be written in terms of the field $\boldsymbol{P}(\boldsymbol{x})$ expressed as

$$\boldsymbol{P}(\boldsymbol{x}) = \int \mathrm{d}^3\boldsymbol{x}'\, \boldsymbol{g}(\boldsymbol{x}, \boldsymbol{x}')\rho(\boldsymbol{x}'), \tag{2.13}$$

where $\boldsymbol{g}(\boldsymbol{x}, \boldsymbol{x}')$ is *any* Green's function solution of the equation,

$$\nabla_{\boldsymbol{x}} \cdot \boldsymbol{g}(\boldsymbol{x}, \boldsymbol{x}') = -\delta^3(\boldsymbol{x} - \boldsymbol{x}'). \tag{2.14}$$

$A[\boldsymbol{P}]$, (2.8), is thus also a functional of $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')$, which we denote by $A[\boldsymbol{g}]$ (cf. (4.18) below). In this way the transformation induced by Λ, equation (2.8), can be extended to a family of unitary transformations parametrized by the arbitrary non-local vector field $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')$ that satisfies (2.14).

The generalized PZW approach has the benefit of showing directly how the interaction Hamiltonian in an arbitrary gauge can be simply related to the familiar Coulomb gauge interaction (2.1); the latter is obtained when the Green's function $\boldsymbol{g}$ is chosen to be purely longitudinal ($\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')^{\perp}=\boldsymbol{0}$). If we write (2.1) in the form,

$$H[0]_{\text{int}} = V_1[0] + V_2[0], \tag{2.15}$$

where the subscripts refer to the powers of the coupling constant e and the [0] refers to $\boldsymbol{g}^{\perp}=\boldsymbol{0}$ in this gauge, we have for an arbitrary gauge specified by some non-zero $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')^{\perp}$,

$$H[\boldsymbol{g}]_{\text{int}} = V_1[\boldsymbol{g}^{\perp}] + V_2[\boldsymbol{g}^{\perp}], \tag{2.16}$$

where, from (2.9),

$$\left.\begin{aligned} V_1[\boldsymbol{g}^{\perp}] &= V_1[0] + \frac{\mathrm{i}}{\hbar}[H_0, A[\boldsymbol{g}^{\perp}]], \\ V_2[\boldsymbol{g}^{\perp}] &= V_2[0] + \frac{\mathrm{i}}{\hbar}[V_1[0], A[\boldsymbol{g}^{\perp}]] + \frac{1}{2!}\left(\frac{\mathrm{i}}{\hbar}\right)^2 [[H_0, A[\boldsymbol{g}^{\perp}]], A[\boldsymbol{g}^{\perp}]], \end{aligned}\right\} \tag{2.17}$$

and H_0 is given by (2.6), (2.7).

The full Hamiltonian can also be obtained by canonical quantization of a suitable Lagrangian written in terms of $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')$ (Woolley 1999). The general vector potential $\boldsymbol{a}(\boldsymbol{x})$ is related to the Coulomb gauge vector potential $\boldsymbol{A}(\boldsymbol{x})$ by

$$\boldsymbol{a}(\boldsymbol{x}) = \boldsymbol{A}(\boldsymbol{x}) - \nabla_{\boldsymbol{x}} \int \mathrm{d}^3\boldsymbol{x}'\, \boldsymbol{A}(\boldsymbol{x}') \cdot \boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}'). \tag{2.18}$$

The interaction Hamiltonian, however, is *not* simply (2.1) written in the arbitrary gauge (2.18) (Woolley 1996). The initial step in canonical quantization is the development of a general classical Hamiltonian that is fully equivalent to the conventional Maxwell–Lorentz formulation of classical electrodynamics; this Hamiltonian contains the term $\int \mathrm{d}^3\boldsymbol{x}\, |\boldsymbol{P}(\boldsymbol{x})^{\perp}|^2$, which involves the arbitrary $\boldsymbol{g}^{\perp}$. $A[\boldsymbol{P}]$, equation (2.8), interpreted as a classical quantity, is the generator of the classical canonical transformation corresponding to the (generalized) quantum PZW transformation. The canonical quantization procedure leads to the same Hamiltonian as the generalized PZW transformation of the quantized Coulomb gauge theory (Woolley 1999).

These two approaches can also be applied to the semi-classical model where the field is taken to be classical and only the charges are quantized. It is clear, however, that in the quantum PZW theory the term $\int \mathrm{d}^3\boldsymbol{x}\, |\boldsymbol{P}(\boldsymbol{x})^{\perp}|^2$ arises in $V_2[\boldsymbol{g}^{\perp}]$ from the second commutator in (2.17) because the field operators $\boldsymbol{A}(\boldsymbol{x})$ and $\boldsymbol{E}(\boldsymbol{x}')^{\perp}$ do not commute; it is essential in quantum theory in any gauge other than the Coulomb gauge (in which it vanishes identically) for the maintenance of gauge invariance for processes involving states in which the photon occupation numbers do not change. There is no such contribution from the corresponding classical fields $\boldsymbol{A}(\boldsymbol{x})$ and $\partial\boldsymbol{A}(\boldsymbol{x})/\partial t$, so a semiclassical PZW transformation generated by (2.8) with the classical field $\boldsymbol{A}(\boldsymbol{x})$ does not produce this term, and the interaction term of $O(e^2)$ in the Hamiltonian cannot be specified unambiguously. Thus the semiclassical approximation is itself gauge dependent because the two ways of obtaining its Hamiltonian only agree in the Coulomb gauge; in any other gauge there are two different semiclassical Hamiltonians which differ by the integral $\int \mathrm{d}^3\boldsymbol{x}\,|\boldsymbol{P}(\boldsymbol{x})^{\perp}|^2$. This makes a discussion of the gauge invariance of the semiclassical radiation model problematic.

In summary, $H[\boldsymbol{g}]$ is a general Hamiltonian parametrized by the field $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')^{\perp}$ that is very convenient for investigating the gauge invariance of calculated quantities; a necessary condition for such quantities to be identified with physical observables is that they be independent of $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')^{\perp}$. Of course since $\Lambda[\boldsymbol{g}]$ is unitary, the family of Hamiltonians $H[\boldsymbol{g}]$ must share certain invariants independent of the representation specified by $\boldsymbol{g}(\boldsymbol{x},\boldsymbol{x}')$, notably their eigenvalue spectra and S-matrix elements. In the following we discuss how these properties behave in approximate calculations based on different forms of perturbation theory.

3. The *S*-matrix: non-resonant case

The customary division of the full non-relativistic Hamiltonian into a reference Hamiltonian, H_0, and an interaction Hamiltonian, V,

$$H = H_0 + V \tag{3.1}$$

shown explicitly in (2.1), (2.3), (2.5)–(2.7), (2.17), is not a gauge-invariant separation because of the dependence of V on $\boldsymbol{g}^{\perp}$. The requirement that calculated physical observables must be gauge invariant is an important constraint on any proposed quantum mechanical calculation. We have recently studied the perturbation theory for the S-matrix associated with the general Hamiltonian $H[\boldsymbol{g}]$ in a time-independent framework, and have shown that on the energy shell, S-matrix elements are gauge invariant in every order of perturbation theory (Woolley 1998). The idea of this proof by induction can be applied to other theoretical approaches, so we briefly outline the method.

If we use H_0 to define a basis set,

$$H_0\Phi_i = E_i\Phi_i, \tag{3.2}$$

the Lippmann–Schwinger equations show that the S-matrix in this basis has the form (Roman 1965)

$$S_{fi} = \delta_{fi} - 2\pi\mathrm{i}\delta(E_f - E_i)T_{fi}, \tag{3.3}$$

where the transition matrix T satisfies the formal operator relation,

$$T = V + VG_0^+T. \tag{3.4}$$

G_0^+ is a Green's function for H_0

$$G_0^+ = \frac{1}{E - H_0 + \mathrm{i}\varepsilon} \tag{3.5}$$

and T_{fi} in (3.3) is to be evaluated at $E = E_i$.

Let λ stand for the coupling constant in the interaction—here the electron charge e. The dependence of V on λ is then, from (2.15)–(2.17),

$$V = \lambda V_1 + \lambda^2 V_2. \tag{3.6}$$

We write T as a perturbation series in λ

$$T = \sum_n \lambda^n T^{(n)} \tag{3.7}$$

and combining (3.4) with (3.6), (3.7) leads to a recurrence relation for the $T^{(n)}$

$$T^{(n)} = V_1 G_0^+ T^{(n-1)} + V_2 G_0^+ T^{(n-2)} \tag{3.8}$$

with starting values,

$$T^{(1)} = V_1, \tag{3.9}$$

$$T^{(2)} = V_2 + V_1 G_0^+ T^{(1)}. \tag{3.10}$$

Now consider this recursion for two different gauges specified by $\boldsymbol{g}^{\perp} = \mathbf{0}$, and some non-zero $\boldsymbol{g}^{\perp}$. Let the corresponding T-matrices be denoted by $T[0]$ and $T[\boldsymbol{g}]$, and write their difference as

$$W[\boldsymbol{g}] = T[\boldsymbol{g}] - T[0]. \tag{3.11}$$

$W[\boldsymbol{g}]$ can also be expanded as a perturbation series,

$$W[\boldsymbol{g}] = \sum_n \lambda^n W[\boldsymbol{g}]^{(n)} \tag{3.12}$$

and we can easily derive a recurrence relation for the $W^{(n)}$ from that for the $T^{(n)}$. The proof of the gauge invariance of the S-matrix rests on the result that, for all n, the $W^{(n)}$ can be written as a commutator involving H_0,

$$W[\boldsymbol{g}]^n \equiv [H_0, \Omega[\boldsymbol{g}]^n], \tag{3.13}$$

where the $\Omega^{(n)}$ are given explicitly elsewhere (Woolley 1998). The difference between T-matrix elements (3.11) in the basis defined by (3.2), thus depends on

$$W[\boldsymbol{g}]^n_{fi} = (E_f - E_i)\Omega[\boldsymbol{g}]^n_{fi} \tag{3.14}$$

and this is annihilated by the energy conservation delta function in (3.3) provided Ω does not have a pole at energy E_i; the S-matrix is then gauge-invariant (independent of $\boldsymbol{g}^{\perp}$) in all orders of perturbation theory.

There are several ingredients that are essential for the success of the argument. Firstly, the assumption that the perturbation series is meaningful is at best of only limited validity. The occurrence of intermediate states that are degenerate with the initial state Φ_i makes $G_0^+(E_i)$ singular, and requires particular attention; this is important for resonance phenomena of course. Next, the reduction of the gauge-dependent terms to the commutator (3.13) depends on *complete sets* of intermediate states being used in the evaluation of the perturbation series. Thus we may expect gauge-dependence problems in perturbation theories in which specified intermediate states are to be omitted from the matrix multiplications, since this can lead to incomplete cancellation of gauge-dependent terms. Some examples are given below. Finally, the energy conservation condition for the process $i \to f$, which makes (3.14) vanish, is crucial for the argument to work; energy conservation is only required for real processes, and virtual processes which appear in perturbation theories have to be treated carefully if gauge dependence is to be avoided.

4. Time-dependent perturbation theory

An important class of time-dependent calculations used in electrodynamics can be formulated as follows. We seek a solution of the time-dependent Schrödinger equation,

$$\mathrm{i}\hbar\frac{\partial|\Psi\rangle}{\partial t} = H|\Psi\rangle, \tag{4.1}$$

subject to an initial condition that specifies $\Psi(t=0)$ as an eigenstate Φ_p of H_0, (3.2), and then examine the solution for later times t; the method of solution involves transforming to an interaction representation by setting

$$|\Psi(t)\rangle = \mathrm{e}^{-\mathrm{i}H_0 t/\hbar}|\Phi(t)\rangle. \tag{4.2}$$

The projections of the eigenstates of the reference system $\{\Phi_i\}$ on $|\Phi(t)\rangle$ are the development coefficients $\{b(t)_i\}$ of the traditional method of variation of constants.

As is well known, a non-perturbative formal solution of the problem can be obtained by introducing a Fourier integral representation with

$$b(t)_k = -\frac{1}{2\pi\mathrm{i}}\int_{-\infty}^{+\infty} A(E)_k \mathrm{e}^{\mathrm{i}(E_k-E)t/\hbar}\,\mathrm{d}E; \tag{4.3}$$

$A(E)_k$ is a meromorphic function of E with its poles lying in the lower-half complex E-plane so as to ensure that $b(t)_k = 0$ for $t < 0$. If we define the matrix $\boldsymbol{U}(E)$ as the solution of the implicit equation

$$[\boldsymbol{U}(E)]_{kp} = [\boldsymbol{V}]_{kp} + [\boldsymbol{V}\boldsymbol{G}_0^+(E)\boldsymbol{U}(E)]_{kp} \tag{4.4}$$

with the understanding that the initial state p is omitted from the matrix multiplication in (4.4), then the coefficients $\{A(E)_k\}$ are

$$A(E)_p = \frac{1}{E - E_p - U(E)_{pp}}, \tag{4.5}$$

$$A(E)_k = U(E)_{kp}\frac{1}{E - E_k + \mathrm{i}\varepsilon}A(E)_p, \qquad k \neq p. \tag{4.6}$$

In modern terminology these coefficients are matrix elements of the resolvent of H (Heitler 1954; Hameka 1965; Roman 1965; Faisal 1987; Blake 1990). In practice, of course, this solution can usually only be applied using an expansion of $\boldsymbol{U}(E)$ in powers of the interaction V, and it is this expansion we discuss below using the general Hamiltonian (§ 2).

The computation of the Fourier integral (4.3) is in general highly complicated because $\boldsymbol{U}(E)$ does not have a simple dependence on the variable E. Two main approximations have been used. Firstly, the probability for a transition $\Phi_p \to \Phi_k$, given by

$$P_k = |b(+\infty)_k|^2, \tag{4.7}$$

requires the limiting value for $t \to +\infty$. A straightforward calculation (Heitler 1954) yields the asymptotic values,

$$b(+\infty)_k = \frac{U(E_k)_{kp}}{E_k - E_p - U(E_k)_{pp}}, \qquad k \neq p, \tag{4.8}$$

$$b(+\infty)_p = 0. \tag{4.9}$$

For studying the time evolution of the system at finite times, the resonant state on-the-energy-shell approximation has been invoked. This amounts to the claims that the energy correction term $U(E)_{pp}$ is a slowly varying function of E close to E_p and that the real part of this term will be much smaller than E_p. There is then a pole in $A(E)_p$ close to E_p and to sufficient accuracy $A(E)_p$ may be approximated by $A(E_p + \mathrm{i}\varepsilon)$, with the usual limit $\varepsilon \to 0^+$ understood (Blake 1990).

Comparison of the matrix $\boldsymbol{U}(E)$, (4.4), with the T-matrix (3.4) shows that they have similar structures, and we make a corresponding analysis of $\boldsymbol{U}(E)$. For example, instead of (3.9), (3.10) we have

$$U^{(1)} = V_1, \tag{4.10}$$

$$U^{(2)} = V_2 + V_1 G_0^+ U^{(1)}. \tag{4.11}$$

There are, however, two essential differences: firstly, $\boldsymbol{U}(E)$ is not required at $E = E_p$ (the initial state energy); and, secondly, there is a restriction on the sum over states in the matrix multiplication in (4.6) that does not apply to (3.4).

As in § 3, (4.10) and (4.11) can be compared for two different gauges; a non-zero matrix element for this difference, which we call $K(E, [\boldsymbol{g}])$, signals gauge dependence of the corresponding matrix element of $\boldsymbol{U}(E)$. Equation (4.10) with (2.17) leads at once to the first-order result,

$$K(E, [\boldsymbol{g}])^{(1)} \equiv U(E, [\boldsymbol{g}])^{(1)} - U(E, [0])^{(1)} \tag{4.12}$$

$$= \frac{\mathrm{i}}{\hbar}[H_0, A], \tag{4.13}$$

where from now on we do not show explicitly the dependence of A on $\boldsymbol{g}(\boldsymbol{x}, \boldsymbol{x}')$. Similarly, taking the difference between the terms in (4.11) for two different gauges leads to

$$K(E, [\boldsymbol{g}])^{(2)} \equiv U(E, [\boldsymbol{g}])^{(2)} - U(E, [0])^{(2)} \tag{4.14}$$

$$= V_2[\boldsymbol{g}] - V_2[0] + V_1[\boldsymbol{g}]G_0^+ U(E, [\boldsymbol{g}])^{(1)} - V_1[0]G_0^+ U(E, [0])^{(1)}; \tag{4.15}$$

with the aid of (2.17) and (4.12) this reduces to

$$-\mathrm{i}\hbar K(E, [\boldsymbol{g}])^{(2)} = [V_1[0], A] + V_1[0]G_0^+[H_0, A] + [H_0, A]G_0^+ V_1[0] + \frac{\mathrm{i}}{\hbar}[H_0, A]G_0^+[H_0, A] - \frac{1}{2}\frac{\mathrm{i}}{\hbar}[A, [H_0, A]]. \tag{4.16}$$

Physical applications based on equation (4.7) have their gauge dependence contained in the (k, p) and (p, p) matrix elements of $K(E_k, [\boldsymbol{g}])$. In first order we have

$$K(E_k, [\boldsymbol{g}])^{(1)}_{kp} = \frac{\mathrm{i}}{\hbar}(E_k - E_p)A_{kp}. \tag{4.17}$$

From (2.8), (2.13) the explicit form for A is

$$A[\boldsymbol{g}] = \int \mathrm{d}^3\boldsymbol{x} \int \mathrm{d}^3\boldsymbol{x}'\, \boldsymbol{A}(\boldsymbol{x}) \cdot \boldsymbol{g}(\boldsymbol{x}, \boldsymbol{x}')\rho(\boldsymbol{x}'). \tag{4.18}$$

The Coulomb gauge vector potential has non-zero matrix elements between states differing by one photon (Heitler 1954; Power 1964), so both factors in (4.17) vanish in the diagonal element, $k = p$, but matrix elements of $K(E_k, [\boldsymbol{g}])_{kp}$ between states k, p differing by one photon are in general gauge dependent unless they are degenerate. The matrix elements of the second-order term are easily found; they are

$$-\mathrm{i}\hbar K(E_k, [\boldsymbol{g}])^{(2)}_{kp} = (E_k - E_p)\left((V_1[0]G_0^+(E_k)A)_{kp} + \frac{1}{2}\frac{\mathrm{i}}{\hbar}(AA)_{kp}\right), \qquad k \neq p, \tag{4.19}$$

and

$$K(E_k, [\boldsymbol{g}])^{(2)}_{pp} = -\frac{2}{\hbar}(E_k - E_p)\,\mathrm{Im}\,(V_1[0]G_0^+(E_k)A)_{pp} - \frac{(E_k - E_p)}{\hbar^2}\sum_m \frac{E_{pm}A_{pm}A_{mp}}{E_{km}}, \tag{4.20}$$

which is purely real. One can continue in this fashion for higher terms but the pattern is already clear; gauge invariant probabilities (4.7) are only obtained if a condition of energy conservation ($E_k = E_p$) is imposed from outside the theory. Otherwise, the gauge-dependent terms in the numerator ($U(E_k)_{kp}$) and denominator ($U(E_k)_{pp}$) of (4.8) are non-zero (and arbitrary).

These calculations can be applied directly to the diagonal matrix element of the resolvent, $A(E)_p$, (4.5) at arbitrary energy E. The first non-zero gauge-dependent term in a perturbation series for $U(E)_{pp}$ is (4.20) with E_k replaced by E. Assuming that the coefficients of $(E - E_p)$ in (4.20) are regular, this vanishes at $E = E_p$, so that the *final result* of the resonant state on-the-energy-shell approximation (Blake 1990) is gauge invariant. However, the arbitrariness of these coefficients spoils the argument that $U(E, [\boldsymbol{g}])_{pp}$ must be small compared with E_p for E near E_p, irrespective of $\boldsymbol{g}$, and the pole need not be close to E_p. Of course, the true poles of $A(E)_{pp}$ are the eigenvalues of the full Hamiltonian H (Roman 1965), which are gauge invariant, so the difficulty lies in the use of this perturbation series.

An account of the interactions of molecules with quantized radiation including one- and two-photon absorption and emission, scattering of photons, and spectral line-shape theory including resonance fluorescence can be based on (4.3)–(4.9) (Hameka 1965). For the calculation of transition probabilities per unit time the matrix $\boldsymbol{U}(E)$ is required on the energy shell and gives gauge-invariant results. For other applications such as the scattering of photons, however, approximate energy conservation was invoked only through the claim that the real and imaginary parts of the diagonal element U_{pp} are 'small' relative to typical molecular excitation energies. As above, this argument is invalidated by the gauge dependence of $\boldsymbol{U}$ when energy conservation is not strictly valid; the gauge-dependent terms in $\boldsymbol{U}$ are unbounded and so the magnitude of $\boldsymbol{U}$ is completely arbitrary.

Another application of the time-dependent theory described here is the conventional account of the shapes of spectral lines, particularly for emission lines and resonance fluorescence (Heitler 1954; Power & Zienau 1959; Hameka 1965; Landau & Lifshitz 1971). This formalism is taken to be a theoretical improvement over the original treatment of Weisskopf & Wigner (1930) (see also Sakurai 1967, 1994), which starts from the assumption that the initial state decays exponentially in time, and does not allow for any frequency variation of the matrix elements involved. A typical calculation is the theory of the natural lineshape which can be obtained by taking the initial state at $t = 0$, Φ_p, to describe an excited atomic level with energy $\mathcal{E}_n$ and no photons present, while Φ_k refers to the atom in its ground state, energy $\mathcal{E}_0$, and a photon of frequency ω is present. The required probability for emission of a photon in the frequency interval $[\omega, \omega + \mathrm{d}\omega]$ is then

$$\mathrm{d}w = |b(+\infty)_{kp}|^2 \,\mathrm{d}\omega \tag{4.21}$$

and has the form (Landau & Lifshitz 1971)

$$\frac{|U(E_k)_{kp}|^2 \,\mathrm{d}\omega}{(\omega - \omega_{no})^2 + \Gamma^2/4}, \tag{4.22}$$

where ω_{no} is the separation of the atomic levels, and Γ is the decay constant defined by $\frac{1}{2}\hbar\Gamma = \mathrm{Im}\, U(E_k)_{pp}$. It is usually argued that since $\Gamma \ll \omega$ we can put

$$\mathcal{E}_n - \mathcal{E}_o = \hbar\omega, \tag{4.23}$$

i.e. take $E_k = E_p$, which would ensure gauge invariance. This argument is spoilt by the gauge dependence of the denominator implied by (4.20).

With narrow bandwidth radiation sources, moreover, the frequency variation of the lineshape can be measured accurately; it is not completely determined by the denominator in (4.22). This was investigated in detail by Power & Zienau (1959), who considered a variety of lineshape problems including the experiment for the accurate determination of the Lamb shift in hydrogen (Lamb 1952). They showed that the Coulomb gauge theory (in dipole approximation) and the multipole Hamiltonian, restricted to its first, electric dipole, term gave different frequency dependencies as ω moved away from the resonance condition (4.23) because of the frequency variation of the numerator of (4.22). From the present perspective this difference is simply the expected result of the gauge dependence of $U(E_k)_{kp}$ when $E_k \neq E_p$, and it suggests that an entirely different method of calculation that maintains gauge invariance throughout must be sought for the lineshape observable. This is so even though it appears that the multipole Hamiltonian leads to a predicted lineshape in good agreement with Lamb's experiment (Lamb 1952; Power & Zienau 1959) which is sufficiently precise to rule out definitely the Coulomb gauge calculation; this result remains to be explained.

In terms of the usual unitary time evolution operator $U(t, t_0)$ we have

$$|\Phi(t)\rangle = U(t, t_0)|\Phi(t_0)\rangle. \tag{4.24}$$

and so, from (4.24), and the given initial conditions

$$b(t)_k = \langle\Phi_k|U(t, 0)|\Phi_p\rangle, \tag{4.25}$$

which shows $U(t, 0)$ to be essentially the Fourier transform of the resolvent $A(E)$ in (4.5), (4.6). It is known from general formal considerations (Weinberg 1995) that *only* in the doubly infinite limit $t_0 \to -\infty$, $t \to +\infty$, do the matrix elements of $U(t, t_0)$ have the property

$$\langle\Phi_k|U(+\infty, -\infty)|\Phi_p\rangle \propto \delta(E_k - E_p); \tag{4.26}$$

otherwise, as found above, matrix elements of $U(t_0, t)$ do not enforce energy conservation, which appears to be intimately involved in the maintenance of gauge invariance. This leads to a requirement that the initial and final states in *physical processes* must be stable (Cohen-Tannoudji *et al.* 1989). These calculations cast serious doubt as to whether physically meaningful (gauge invariant) time-dependent probabilities can actually be obtained for processes involving electromagnetic radiation. Evident weaknesses of these calculations are the unphysical initial condition which specifies that the atomic system is in a sharp energy eigenstate of H_0 at the initial instant $t = 0$, and, in the lineshape calculations, the specification of states liable to decay by spontaneous emission.

5. *S*-matrix theory and resonance

An obvious candidate for a replacement for the time-dependent theory discussed in § 4 is some version of S-matrix theory; the natural lineshape was already considered by Low (1952) within the covariant QED formalism, although that method has never been extended to a general account of resonant molecular light scattering and the general problem of line broadening. It was pointed out by Fried (1973) that at least part of the difficulty identified by Power & Zienau (1959) in non-relativistic lineshape theory could be avoided if the non-resonant part of the cross-section was also retained. In fact, as we shall see, dividing the T-matrix up into resonant and non-resonant contributions is a gauge-dependent separation which leads to the difficulties encountered in practical applications.

The exact Green's function for H, (3.1), satisfies the operator equation,

$$G^+(E) = G_0^+(E) + G_0^+(E)VG^+(E) \tag{5.1}$$

and using $G^+(E)$ we can write the transition matrix in closed form (Roman 1965)

$$T(E) = V + VG^+(E)V. \tag{5.2}$$

In terms of matrix elements for a transition $\Phi_i \to \Phi_f$, these equations yield

$$T(E_i)_{fi} = V_{fi} + \sum_{m,n} V_{fm}G^+(E_i)_{mn}V_{ni} \tag{5.3}$$

with

$$G^+(E_i)_{mn} = \frac{\delta_{mn}}{E_i - E_m + \mathrm{i}\varepsilon} + \frac{1}{E_i - E_m + \mathrm{i}\varepsilon}\sum_k V_{mk}G^+(E_i)_{kn}. \tag{5.4}$$

Iteration of (5.4) with (5.2) leads to the perturbation series for T reviewed in § 3.

Suppose now that for some $m = p$ we have $E_p = E_i$, so that the iteration of (5.4) cannot be expected to converge. The customary procedure is to isolate this term and write (5.3) as a sum of 'resonant' and 'non-resonant' contributions:

$$T_{fi} = T_{fi}^{\text{res}} + T_{fi}^{\text{non-res}} \tag{5.5}$$

with

$$T_{fi}^{\text{res}} = V_{fp}G^+(E_i)_{pp}V_{pi}, \tag{5.6}$$

$$T_{fi}^{\text{non-res}} = V_{fi} + \sum_{m,n}(1 - \delta_{mn}\delta_{np})V_{fm}G^+(E_i)_{mn}V_{ni}. \tag{5.7}$$

Assuming there are no other resonances, the usual perturbation series is taken to be sufficient for the non-resonant contribution

$$T_{fi}^{\text{non-res}} \approx V_{fi} + \sum_{m \neq p} \frac{V_{fm} V_{mi}}{E_i - E_m + \mathrm{i}\varepsilon} + \cdots . \tag{5.8}$$

On the other hand, a more exact treatment is required for the resonant contribution; because of level shifts and radiation damping, the singularity at $E_i = E_p$ in $G_0^+(E_i)$ is shifted to a complex pole in $G^+(E_i)$, which gives rise to the characteristic resonance lineshape in spectra.

Let us first consider the non-resonant contribution in two different gauges, i.e. evaluate

$$T[\boldsymbol{g}]_{fi}^{\text{non-res}} - T[0]_{fi}^{\text{non-res}}. \tag{5.9}$$

This calculation is obviously closely related to the proof of gauge invariance of the S-matrix outlined in § 3, but there is now a difference due to the omission of the state Φ_p from the matrix multiplications. It is sufficient to write out (5.9) to $O(\mathrm{e}^2)$ using (5.8) to see the nature of the problem; the difference between the perturbation in the two gauges yields, from (2.17),

$$\left.\begin{aligned} V[\boldsymbol{g}] - V[0] &\equiv \Delta[\boldsymbol{g}], \\ \Delta[\boldsymbol{g}] = \left(\frac{\mathrm{i}}{\hbar}\right)[H_0, A] + \left(\frac{\mathrm{i}}{\hbar}\right)&[V_1[0], A] + \frac{1}{2!}\left(\frac{\mathrm{i}}{\hbar}\right)^2 [[H_0, A], A]. \end{aligned}\right\} \tag{5.10}$$

The (fi) matrix element of the first term in (5.10) vanishes on the energy shell, $E_f = E_i$, but the elimination of the remaining two terms requires cancellation by compensating terms that must originate from the second term in (5.8). Unlike the situation in § 3, this cancellation is *not* complete, however, because of the deletion of the state Φ_p from the matrix multiplication in the second term. A straightforward calculation shows that to $O(\mathrm{e}^2)$ (5.9) reduces to

$$\frac{\mathrm{i}}{\hbar}(V_{fp} A_{pi} - A_{fp} V_{pi}), \tag{5.11}$$

which does not generally vanish and can therefore have any value. Obviously, the 'missing term' required to cancel (5.11) would have been found in (5.6) if we could have assumed $E_p \neq E_i$, and replaced $G^+(E_i)$ by $G_0^+(E_i)$; however, the more complete treatment of the Green's function $G^+(E_i)$ spoils this relationship.

Standard formal manipulations in resolvent theory (Roman 1965) show that

$$G^+(E_i)_{pp} = \frac{1}{E_i - E_p - \Sigma(E_i)_{pp}}, \tag{5.12}$$

where

$$\begin{aligned} \Sigma(E_i)_{pp} &= \langle \Phi_p | \{V + V G_0^+(E_i) V \ldots\}' | \Phi_p \rangle \\ &= \{V + V G_0^+(E_i) \Sigma(E_i)\}_{pp}; \end{aligned} \tag{5.13}$$

the state Φ_p is to be excluded from the matrix multiplications in (5.13). Clearly, the dependence of $\boldsymbol{\Sigma}$ on $\boldsymbol{g}$ can be investigated using the iteration method (Woolley 1998) briefly reviewed in § 3. Comparison of (4.4) and (5.13) shows, however, that $\boldsymbol{\Sigma}(E)$ and $\boldsymbol{U}(E)$ are the same operator quantity (i.e. (5.12) is the same as the diagonal element $A(E)_p$, (4.7)), and it is sufficient to use the discussion of gauge dependence in § 4 by replacing E_k with E_i as appropriate. We then have the immediate result that to second order $\Sigma(E_i)_{pp}$ is gauge-invariant, when we invoke the resonance condition $E_i = E_p$ in equation (4.20). This, however, is not sufficient to ensure that the separation of the T-matrix in (5.5) leads to a gauge-invariant result as can be seen by looking at the gauge dependence of the numerator in the pole term in two different gauges,

$$T_{fi}[\boldsymbol{g}]^{\text{res}} - T_{fi}[0]^{\text{res}} = \{V[\boldsymbol{g}]_{fp}V[\boldsymbol{g}]_{pi} - V[0]_{fp}V[0]_{pi}\}\frac{1}{E_i - E_p - \Sigma(E_i)_{pp}}. \tag{5.14}$$

Introducing $\Delta[\boldsymbol{g}]$ from (5.10) the numerator term in braces comes down to

$$V[0]_{fp}\Delta[\boldsymbol{g}]_{pi} + \Delta[\boldsymbol{g}]_{fp}V[0]_{pi} + \Delta[\boldsymbol{g}]_{fp}\Delta[\boldsymbol{g}]_{pi}. \tag{5.15}$$

The lowest-order contribution, proportional to e^2, vanishes because the resonance condition $E_f = E_i = E_p$ removes the (fp) and (pi) matrix elements of the H_0 commutator term in $\Delta[\boldsymbol{g}]$, assuming that $\Sigma(E_i)_{pp} \not\simeq 0$ in the denominator of (5.14). This means that the contribution required to cancel (5.11) in the non-resonant part of the T-matrix is lost. On the other hand there are gauge-dependent and generally non-zero contributions of order e^3 and e^4 in (5.15) which do not cancel out with compensating terms of the same order in $T_{fi}^{\text{non-res}}$ because they are multiplied with $G^+(E_i)_{pp}$ rather than $G_0^+(E_i)_{pp}$. It is very difficult to see how one can make a consistent gauge invariant calculation of the T-matrix T_{fi} if one starts by isolating the pole associated with a resonance.

A solution to this problem can, however, be achieved by a refinement of the scattering formalism summarized in § 3 (Goldberger 1951; Bethe & de Hoffmann 1954). Instead of writing the T-matrix in terms of the solution of the integral equation (3.4), the problem is divided into two parts; it is convenient to use the notational convention that subscripts i, f, n will be used to designate states of the *same* energy $E_i = E_f = E_n = E$, and subscripts α, β denote states for which E_α, $E_\beta \not\simeq E$. The T-matrix on the energy shell is related to an auxiliary matrix $\boldsymbol{D}$ by an equation also known as the Heitler integral equation,

$$T_{fi} = D_{fi} - \mathrm{i}\pi\sum_n D_{fn}\delta(E - E_n)T_{ni}; \tag{5.16}$$

the equation that determines the damping matrix $\boldsymbol{D}$ involves general off-energy-shell matrix elements

$$\mathcal{D}_{\beta i} = V_{\beta i} + (VG_0^{\mathrm{P}}(E_i)\mathcal{D})_{\beta i} \tag{5.17}$$

with G_0^{P} the standing-wave Green's function for H_0 (the superscript 'P' stands for Cauchy principal value)

$$G_0^{\mathrm{P}}(E_i) = \frac{P}{E_i - H_0} \equiv \frac{1}{2}\left(\frac{1}{E_i - H_0 + \mathrm{i}\varepsilon} + \frac{1}{E_i - H_0 - \mathrm{i}\varepsilon}\right). \tag{5.18}$$

$\mathcal{D}$ is obviously closely related to the matrix $\boldsymbol{U}$ in (4.4); only its on-energy-shell elements $\boldsymbol{D}$ are required for the scattering amplitude, T, and from the previous analysis of the gauge dependence of $\boldsymbol{U}$, these can be seen to be gauge invariant. T and $\boldsymbol{D}$ commute and so can be brought to diagonal form by the same similarity transformation. If the eigenvalues of $\boldsymbol{D}$ are $\{d_I\}$, the T-matrix has eigenvalues

$$t_I = \frac{d_I}{1 - \mathrm{i}\pi d_I}, \tag{5.19}$$

which shows that an iteration solution of (5.16) is convergent for

$$(d_I^{\max})^2 < \frac{1}{\pi^2}. \tag{5.20}$$

The denominator in (5.19) describes the radiation damping and energy shifts associated with resonance phenomena.

6. Discussion

The development of a general non-relativistic Hamiltonian for atoms and molecules interacting with electromagnetic radiation has proved very convenient for the investigation of the gauge invariance properties of different methods of calculation. The conventional formulations that are restricted to one of two gauges (Coulomb, multipole) offer little scope for understanding what is required of a calculation method for it to be gauge invariant. Such gauge choices have often been presented as being necessary for the explicit separation of the Coulombic interaction between the charges that must be put into the unperturbed atomic Hamiltonian, H_{C}, equation (2.6). However, (2.18) shows that there are infinitely many gauges for the vector potential that can be used with the unperturbed Hamiltonian, H_0, equations (2.6), (2.7). It thus becomes essential to determine what gauge invariant (i.e. independent of the arbitrary field $\boldsymbol{g}(\boldsymbol{x}, \boldsymbol{x}')$) calculations can be performed.

In an earlier paper the present writer showed that the iteration series for the S-matrix for non-resonant light scattering is gauge invariant in all orders of perturbation theory (Woolley 1998). As shown in § 5 of this paper, the straightforward attempt to generalize this result to the case of resonant scattering by separating explicitly the presumed dominant resonant term from a non-resonant background fails, due to incomplete cancellation of gauge-dependent terms. However, a reorganization of the Lippmann–Schwinger equations through the introduction of the principal value Green's function for H_0 and the Heitler damping matrix, $\boldsymbol{D}$, leads to a gauge-invariant scattering amplitude, equations (5.16), (5.17), so that finally the situation is entirely analogous to covariant QED; the S-matrix is gauge invariant.

As noted in the Introduction, however, many other types of calculation have also been attempted in non-relativistic radiation problems; the general Hamiltonian can be used with these to test for gauge-dependence problems. An obvious example is the use of time-dependent perturbation theory with an initial condition that the system is in some specified state of the free atom + field system at time $t = 0$, which is a standard textbook calculation. However, used with the general Hamiltonian for electrodynamics it yields probability amplitudes $b(t)_k$, equations (4.3)–(4.6), that contain gauge-dependent terms, so it is not the hoped for improvement over the Wigner–Weisskopf ansatz. The Wigner–Weisskopf ansatz yields gauge-invariant amplitudes, and the more general treatment based on the resolvent of H can be modified by hand to obtain similar results. Having said that, it is not at all clear that time-dependent amplitudes $\{b(t)_k\}$ (even for $t \to +\infty$) have any physical significance in radiation problems if they only emerge in gauge-invariant form after approximations have been made.

Much traditional practice is based on the idea of taking a classical limit for the electromagnetic field to give a time-dependent Schrödinger equation for the charges perturbed by a classical, time-dependent field. As shown in § 2, the *form* of the resulting semiclassical Hamiltonian depends on the procedure used to obtain it, except in the Coulomb gauge. In any other gauge there are two different semiclassical Hamiltonians which differ by the term $\int \mathrm{d}^3\boldsymbol{x}\,|\boldsymbol{P}(\boldsymbol{x})^{\perp}|^2$. The presence of this term, which involves the coordinates of the charged particles (see (2.13)), leads to a completely unworkable semiclassical model. The term obviously cannot be included in the atomic Hamiltonian, because it makes the atomic energy levels gauge-dependent; on the other hand, if treated as a perturbation term there are no compensating terms (as there are in QED) to cancel out its gauge-dependent contributions. So on practical grounds one has to exclude it from the semiclassical Hamiltonian, which can thereafter be cast in an arbitrary gauge using the semiclassical PZW transformation generated by (2.8) and (2.13) with the classical Coulomb gauge vector potential $\boldsymbol{A}(\boldsymbol{x})$. Since this is a time-dependent unitary transformation, the gauge invariance of the model can be related to the discussion given by Yang (1976) for charges in the presence of external fields.

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