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# Question of Gauge: Nonresonant Two-Photon Absorption

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The transition probability per unit time for nonresonant two-photon absorption from the 1*s* to the 2*s* state of atomic hydrogen is obtained analytically using both the electric-dipole interaction $-e\vec{E}\cdot\vec{r}$ and the Coulomb-gauge interaction $-(e/m)\vec{A}\cdot\vec{p}$. The two rates are different, except in the case of resonance. In situations like this, gauge invariance can be used to show that results calculated from the $-e\vec{E}\cdot\vec{r}$ interaction are always correct.

I show that in the case of *nonresonant* two-photon absorption by atomic hydrogen, different transition rates are obtained with the electric-dipole interaction $-e\vec{E}\cdot\vec{r}$ and the Coulomb-gauge interaction $-(e/m)\vec{A}\cdot\vec{p}$. This result does not violate gauge invariance, however. Quantum mechanics is indeed gauge invariant, but gauge invariance puts restrictions on the way the Hamiltonian can be broken into an unperturbed part and a perturbation.[1] The gauge-invariant formulation of the interaction of electromagnetic radiation and matter specifies that the electric-dipole interaction $\vec{E}\cdot\vec{r}$ should be used if the atomic Hamiltonian is used as the unperturbed Hamiltonian.[1,2] The electric-dipole interaction $\vec{E}\cdot\vec{r}$ is manifestly gauge invariant, since it involves the electric field $\vec{E}$. This interaction has been called the interaction in the "preferential gauge" by Forney, Quattropani, and Bassani.[3] Lamb[4] found that it was the $\vec{E}\cdot\vec{r}$ interaction that gave agreement with his experiments. On the other hand, the $\vec{A}\cdot\vec{p}$ interaction can be changed by replacing $\vec{A}$ by $\vec{A}+\nabla\Lambda$, where $\Lambda$ is a scalar function which in the Coulomb gauge satisfies Laplace's equation. In the case of *resonant* absorption, where the energy of the final atomic state is exactly equal to the sum of the energies of the initial atomic state and the two photons, we show that the two rates are exactly equal to each other.[5]

A recent Letter[5] on resonant two-photon absorption by atomic hydrogen concluded that either the electric-dipole interaction $\vec{E}\cdot\vec{r}$ or the Coulomb-gauge interaction $\vec{A}\cdot\vec{p}$ could be used for calculating transition probabilities per unit time. A numerical calculation of the second-order transition matrix element was made for the 1*s*-to-2*s* transition in atomic hydrogen. It was shown that to six significant figures the second-order transition matrix element for the two interactions is the same, if both the discrete and continuum states are included in the sum. However, the electric-dipole interaction $\vec{E}\cdot\vec{r}$ gave faster convergence, and its use in numerical calculations was recommended. In a previous paper,[3] the same authors show that in the case of a single-mode field either interaction can be used to calculate the transition

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rates. While this conclusion is valid for resonance, the calculation I give here shows that it is not valid for a nonresonant process.

The Hamiltonian for an electron of charge $e$ in an external electromagnetic field characterized by the vector potential $\vec{A}$ and the scalar potential $A_0$ is

$$H = (1/2m)(\vec{p} - e\vec{A})^2 + V_{ex} + qA_0, \tag{1}$$

where $V_{ex}$ is the static external Coulomb field of the proton. We can make a gauge transformation to a new vector potential

$$\vec{A}' = \vec{A} + \nabla\Lambda, \tag{2}$$

and a new scalar potential

$$A_0' = A_0 - \partial\Lambda/\partial t. \tag{3}$$

If magnetic effects are negligible and the wavelength of the light is large compared to atomic dimensions, the new gauge can be chosen such that

$$\vec{A}' = 0. \tag{4}$$

The gauge function $\Lambda$ can then be calculated from Eq. (2). When it is used in Eq. (3) for the new scalar potential, the electric-dipole interaction,

$$A_0' = -\vec{E}(t)\cdot\vec{r}, \tag{5}$$

is obtained, where $\vec{E} = -\partial\vec{A}/\partial t - \nabla A_0$ is the electric field. In the new gauge the Hamiltonian becomes

$$H' = H_0 - e\vec{E}\cdot\vec{r}, \tag{6}$$

where $H_0 = p^2/2m + V_{ex}$ is the atomic Hamiltonian. The original gauge is usually taken to be the Coulomb gauge ($\nabla\cdot\vec{A} = 0$, $A_0 = 0$), so that Eq. (1) can be written as[6]

$$H = H_0 - (e/m)\vec{A}\cdot\vec{p} + (e^2/2m)\vec{A}^2. \tag{7}$$

The question arises as to whether these two Hamiltonians always give the same result for electric-dipole processes when treated by perturbation theory. The example we consider here of nonresonant two-photon absorption shows that they do not.

The case considered by Bassani, Forney, and Quattropani[5] of two-photon absorption from the $1s$ to the $2s$ state of atomic hydrogen will also be considered here as an example, but any two states could be used. The transition rate for nonresonant absorption of two different photons with frequencies $\omega_1$ and $\omega_2$ is[7]

$$W(1s \to 2s) = |M|^2\Gamma_{2s}/[(E_{2s} - E_{1s} - \omega_1 - \omega_2)^2 + (\Gamma_{2s}/2)^2], \tag{8}$$

where $\Gamma_{2s}$ is the width of the $2s$ state and $M$ is the matrix element. The matrix element for the $\vec{E}\cdot\vec{r}$ interaction is

$$M_r = \sum_n (1 + P_{12}) \frac{\langle 2s|e\vec{E}_2\cdot\vec{r}|n\rangle\langle n|e\vec{E}_1\cdot\vec{r}|1s\rangle}{E_n - E_{1s} - \omega_1}, \tag{9}$$

where $\vec{E}_i$ is the electric-field amplitude of photon $i$ ($i = 1, 2$). The exchange operator that exchanges photon 1 with photon 2 is $P_{12}$. The sum in Eq. (9) is over the continuum states as well as the discrete states.

On the other hand, the matrix element for the $\vec{A}\cdot\vec{p}$ interaction is

$$M_p = \sum_n (1 + P_{12})\langle 2s|(e/m)\vec{A}_2\cdot\vec{p}|n\rangle\langle n|(e/m)\vec{A}_1\cdot\vec{p}|1s\rangle/(E_n - E_{1s} - \omega_1), \tag{10}$$

where $\vec{A}_i$ is the vector potential amplitude of photon $i$ ($i = 1, 2$). This matrix element can be rewritten in terms of $\vec{E}_i$ and $\vec{r}$ by using $\vec{E} = -\partial\vec{A}/\partial t$, the harmonic nature of the field, and the commutation relation $[H_0, \vec{r}] = -i\vec{p}/m$. The matrix element in Eq. (10) then becomes

$$M_p = \sum_n (1 + P_{12}) \frac{\langle 2s|e\vec{E}_2\cdot\vec{r}|n\rangle\langle n|e\vec{E}_1\cdot\vec{r}|1s\rangle}{E_n - E_{1s} - \omega_1} \left[\frac{(E_{2s} - E_n)(E_n - E_{1s})}{\omega_1\omega_2}\right]. \tag{11}$$

In general, $M_p$ in Eq. (11) is not the same as $M_r$ in Eq. (9) for the nonresonant case. Different results will be obtained in general for the $\vec{E}\cdot\vec{r}$ interaction than for the $\vec{A}\cdot\vec{p}$ interaction. The gauge-invariant result is the calculation using the $\vec{E}\cdot\vec{r}$ interaction.[1]

In the nonresonant case energy is not conserved by an amount $\Delta$:

$$E_{2s} = E_{1s} + \omega_1 + \omega_2 + \Delta. \tag{12}$$

Then the energy factors in Eq. (11) can be written as

$$\frac{(E_{2s}-E_n)(E_n-E_{1s})}{\omega_1\omega_2(E_n-E_{1s}-\omega_1)}=\frac{E_{2s}-E_n}{\omega_1\omega_2}-\frac{1}{\omega_2}+\frac{1+\Delta/\omega_2}{E_n-E_{1s}-\omega_1}, \tag{13}$$

and the exchange term can be written as

$$\frac{(E_{2s}-E_n)(E_n-E_{1s})}{\omega_1\omega_2(E_n-E_{1s}-\omega_2)}=\frac{E_{1s}-E_n}{\omega_1\omega_2}+\frac{1}{\omega_2}+\frac{\Delta}{\omega_1\omega_2}+\frac{1+\Delta/\omega_1}{E_n-E_{1s}-\omega_2}. \tag{14}$$

When these expressions are substituted into Eq. (11) the result is

$$M_p=M_r+(1+P_{12})\frac{\Delta}{\omega_2}\sum_n\frac{\langle 2s|e\vec{\mathrm{E}}_2\cdot\vec{\mathrm{r}}|n\rangle\langle n|e\vec{\mathrm{E}}_1\cdot\vec{\mathrm{r}}|1s\rangle}{E_n-E_{1s}-\omega_1}+\frac{\Delta}{\omega_1\omega_2}\langle 2s|(e\vec{\mathrm{E}}_1\cdot\vec{\mathrm{r}})(e\vec{\mathrm{E}}_2\cdot\vec{\mathrm{r}})|1s\rangle. \tag{15}$$

The first term on the right-hand side of Eqs. (13) and (14) combine in Eq. (11) to give zero, when the completeness and orthogonality of the eigenstates of $H_0$ are used, along with the commutation relations. Equation (15) shows that for nonresonance, $\Delta\neq 0$, the matrix element $M_p$ is not equal to $M_r$. For resonance,

$$M_p=M_r \text{ for } \Delta=0.$$

Thus, in the case of resonant two-photon absorption, either interaction may be used,[8] but not in the case of nonresonance. The same conclusions hold for the absorption of radiation by a two-level atom.[2]

The example given here shows that, contrary to a widespread opinion,[9] it does make a difference in some problems whether the $\vec{\mathrm{E}}\cdot\vec{\mathrm{r}}$ interaction or the $\vec{\mathrm{A}}\cdot\vec{\mathrm{p}}$ interaction is used.[10] Correct results will always be obtained in problems in which the electric-dipole approximation can be made if the $\vec{\mathrm{E}}\cdot\vec{\mathrm{r}}$ interaction is used.

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# Spectroscopy of Electronic States in Superheavy Quasimolecules

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We show that information about quasimolecular electronic binding energies in transient atomic systems of $Z=Z_1+Z_2$ up to 184 can be obtained from three sources: (1) the impact-parameter dependence of the ionization probability; (2) the ionization probability in head-on collisions as a function of total nuclear charge $Z$; (3) the delta-electron spectrum in coincidence with $K$-vacancy formation in asymmetric collisions. Experiments are proposed and discussed.

In collisions of very heavy ions $Z_1$ and $Z_2$ it is possible to form quasimolecular systems where the binding energy of the inner-shell electrons is of the order of the electron mass. These systems represent a prototype of highly relativistic, strongly bound quantum systems and have there-