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Question of gauge for the description of two-photon transitions or light scattering when using incomplete sets

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In the calculation of two-photon transition probabilities and related radiation-matter interaction problems, the "length" and "velocity" forms of the dipole interaction give results that can differ by many orders of magnitude if a complete set of exact eigenfunctions is not used. These differences have been illustrated in the case of the $1s$-$2s$ two-photon transition in hydrogen by Bassani, Forney, and Quattropani [Phys. Rev. Lett. 39, 1070 (1977)], and it was concluded by these authors that for this problem the length form of the interaction is far superior to the velocity form when an incomplete set of bound states is used. In order to remove the question of gauge and thereby to improve the accuracy of such calculations when a complete set of exact eigenfunctions is not available, this paper proposes a modified form of the second-order equation. The modified equation, which employs a unique average-frequency approximation, is derived through incorporation of a sum rule that is a direct result of gauge invariance. It contains the length and velocity forms as limiting cases, and, like those equations, is exact for a complete set. Conventional length or velocity equations violate this sum rule for an incomplete set, and therefore are subject to large errors. The use of this modified equation is illustrated for the $1s$-$2s$ transition of hydrogen. Using only the $2p$ state as the "set" of intermediate states, the modified equation yields results that for all photon energies are within 2% of the exact probability amplitudes. For the $1s$-$2s$ problem, the accuracy is comparable to that obtained from length- and velocity-form equations employing an ordinary average-frequency approximation and closure. Unlike the modified equation, however, these latter equations require a separate calculation of matrix elements of r^2 or p^2, which may be inconvenient for a many-electron system. The modified equation should therefore be useful when these matrix elements are not easy to calculate, or when the best gauge form for the problem is not known.

I. INTRODUCTION

In 1977 an important paper by Bassani, Forney, and Quattropani[1] showed that the calculated two-photon transition probability for the hydrogen $1s$-$2s$ transition is independent of whether the "length" $(-q\vec{E}\cdot\vec{r})$ or the "velocity" $(-q/mc)\vec{A}\cdot\vec{p}$ form of the electric dipole interaction is used. This result was obtained by using known dipole matrix elements[2,3] for the complete set of exact eigenfunctions for bound and continuous states of the isolated atom. Though statements to the contrary have been made from time to time,[4] the equivalence of the two forms of the interaction holds to all orders of perturbation theory providing a complete set of exact eigenfunctions (bare or dressed) describing the *true* physical state of the system is employed.[5-7]

A question often addressed[1,8] is "which of the above two forms should be used if a complete set of exact eigenfunctions is not available?" This question permeates many facets of physics—multiphoton spectroscopy,[9] polarizability and light scattering,[10] γ-ray[11] and particle physics,[12] and other problems where perturbation theory is employed to describe the interaction of charged particles and electromagnetic fields.

The purpose of this paper is to present a modified second-order equation that is independent of the gauge question in commonly encountered problems where one does not have a complete set of exact eigenfunctions. Through comparison of exact results for the $1s$-$2s$ two-photon transition of hydrogen, the paper then illustrates advantages of this modified equation compared with conventional equations used for such calculations. Finally, extension of the theory to problems other than the hydrogen atom will be briefly discussed.

II. THEORY (TWO-PHOTON ABSORPTION)

In this and the two subsequent sections, the equations are based on intermediate states that form a complete set. The question of incomplete sets will be raised following these discussions.

If the starting point for the theory is chosen to be the length form of the interaction one has, following Bassani *et al.*,[1]

$$W_{fi}=2\pi\frac{|E_1E_2|^2e^4a_0^4}{4\hbar^4(2\pi\mathscr{R})^3}\frac{1}{9}|D[J_0]|^2\delta(\Delta\omega)\ , \tag{1}$$

where W_{fi} is the two-photon transition probability per atom per unit time, $\mathscr{R}$ is the Rydberg frequency (3.29×10^9 Mc/sec), e is the electronic charge, a_0 is the Bohr radius, and E_1,E_2 are the electric fields associated with the two photons. The frequencies ω in this and subsequent equations have been divided by $2\pi\mathscr{R}$, as in Ref. 1. The argument of the energy-conserving δ function is

$$\Delta\omega=\omega(f)-\omega(i)-\omega_1-\omega_2\ , \tag{2}$$

where i and f label initial and final states of the two-photon transition, and ω_1 and ω_2 are the photon frequencies. Emphasis will be placed on the dimensionless amplitude function[1]

$$D[J_0]=\frac{3}{2}\sum_n(1+P_{12})\frac{\vec{e}_1\cdot\langle f\,|\,\vec{r}/a_0\,|\,n\rangle\langle n\,|\,\vec{r}/a_0\,|\,i\rangle\cdot\vec{e}_2}{\omega(n)-\omega(i)-\omega_2} \tag{3}$$

for $\omega_1,\omega_2\neq[\omega(n)-\omega(i)]$, where $\sum_n$ represents a sum over quantum numbers for the discrete states and integration over those for the continuous spectrum, which together form a complete set. The usual sum over all electrons $\sum_k\vec{r}_k$ for the length operator has been reduced to a single term in (3) in anticipation of dealing with the one-electron problem. The operator P_{12} interchanges the frequencies ω_1,ω_2 and polarizations $\vec{e}_1,\vec{e}_2$ of the two photons. Combining the contributions $(1+P_{12})$ in (3) yields the compact form

$$D[J_0]=\frac{3}{2\omega_1\omega_2}\sum_n F_nC_n\ , \tag{4}$$

useful for algebraic manipulation, where

$$F_n=\frac{\omega_1\omega_2}{[\omega(n)-\omega(i)-\omega_2][\omega(n)-\omega(i)-\omega_1]} \tag{5}$$

and

$$C_n=a_0^{-2}(1+P_{12})(\vec{e}_1\cdot\langle f\,|\,\vec{r}\,|\,n\rangle\langle n\,|\,\vec{r}\,|\,i\rangle\cdot\vec{e}_2)\times[\omega(n)-\omega(i)-\omega_1]\ . \tag{6}$$

The frequency factor F_n given by (5) is characteristic of the length form of the dipole interaction.

If it is desired that the starting point be the velocity form instead of the length form, the above formulation is altered because of a change in the frequency factor

$$D[J]=-\frac{3}{2\omega_1\omega_2}\sum_n F_n'C_n\ , \tag{7}$$

where $D[J]$ is the amplitude function in the velocity form and

$$F_n'=\frac{[\omega(n)-\omega(f)][\omega(n)-\omega(i)]}{[\omega(n)-\omega(i)-\omega_2][\omega(n)-\omega(i)-\omega_1]}\ . \tag{8}$$

Using a bit of straightforward algebra and the energy-shell constraint $\Delta\omega=0$ from (2), it can be shown that the two frequency factors are simply related to one another,

$$F_n'=1-F_n\ . \tag{9}$$

In a case often encountered where $\omega(n)>\omega(f)$, both F_n and F_n' are positive and lie within the range $+0-+1$. Note also that as $\omega(n)\rightarrow\infty$, $F_n\rightarrow0$ while $F_n'\rightarrow1$: the length form emphasizing contributions from low energy states and the velocity form emphasizing those from high-energy states.

III. THEORY (INELASTIC LIGHT SCATTERING)

For light scattering, the scattered photon ("downward transition") can be treated as if it has a negative frequency. Energy conservation is therefore different from (2):

$$\Delta\omega=\omega(f)-\omega(i)-\omega_1+\omega_2\ , \tag{10}$$

where ω_1 is the frequency of the incident photon and ω_2 is the frequency of the scattered photon. There is also a sign reversal of ω_2 following the operation $(1+P_{12})$ in (3) of Sec. II. It follows that

$$F_n'(\mathrm{Sc})=1+F_n(\mathrm{Sc})\ , \tag{11}$$

and the treatment of inelastic light scattering ($i \neq f$) parallels that for two-photon absorption. The remainder of the paper will be concerned only with the two-photon absorption.

IV. THE C_n SUM RULE

Because of the equivalence of the length and velocity forms of the interaction,[7,13] one can equate $D[J_0]$ and $D[J]$ from (4) and (7), which then yields

$$\sum_n F_n C_n + \sum_n F_n' C_n = 0 \ . \tag{12}$$

The relationship (9) between the two frequency factors can therefore be satisfied only when a sum rule,

$$\sum_n C_n = 0 \ , \tag{13}$$

is valid. This sum rule, of course, holds only for a complete set of intermediate states n. This procedure for obtaining (13) is a trivial example of more powerful methods[7] that can be used to obtain interesting sum rules from gauge invariance.

The sum rule (13) can be equivalently derived[14,15] starting with the commutation relationship,

$$\left[H, \sum_{k=1}^{N} \vec{r}_k \right] = -i\hbar \sum_{k=1}^{N} \frac{\vec{p}_k}{m} \ , \tag{14}$$

between length and velocity operators of an N-electron system. The importance here is that the sum rule is a direct result of gauge invariance. Violation of the sum rule is a violation of gauge invariance.

It is well known that the length and velocity forms of the interaction matrix elements often give very different results in the case where an *inexact* set (an incomplete set of states or approximate eigenfunctions) is used. Any result that is not gauge invariant therefore runs the risk of incurring errors that are as large as those associated with switching between the two gauge forms.[16] Conventional second-order amplitude equations, when used with an inexact set, violate the sum rule (13), are not gauge invariant, and are therefore subject to the ambiguity of the gauge question and to unnecessary errors. A question naturally arises about the possibility of modifying the conventional equations so that they do not violate the sum rule when an inexact set of intermediate states is used. If this can be accomplished, one source of error, perhaps a major one, can be removed from such calculations. As shown in Sec. V, it is indeed possible to resolve this question rather simply in at least one way.

V. INEXACT SETS

In most problems in physics, one is not endowed with the luxury of having a complete set of exact eigenfunctions. For consideration of such inexact sets, the contributions to (4) can be split into two parts: $D^c[J_0]$ from "characterized" states and $D^u[J_0]$ from "uncharacterized" states. Characterized states are those for which the exact eigenfunctions or good approximations to them are known, or they may be states for which appropriate spectroscopic constants have been determined experimentally. The spectroscopic constants required are the frequencies and dipole length matrix elements occurring in (3). The uncharacterized states are states in the $\sum_n$ about which nothing is known except that such states are needed to fulfill the sum rule constraint given by (13). Thus,

$$D[J_0] = D^c[J_0] + D^u[J_0]$$
$$= \frac{3}{2\omega_1\omega_2} \left[\sum_n{}^c F_n C_n + \sum_n{}^u F_n C_n \right] \ , \tag{15}$$

where the superscripts c,u label partial sums over characterized and uncharacterized states. F_n is a smoothly varying, transparently convergent function of the frequency $\omega(n)$. On the other hand, C_n contains phase information, and its value is apt to be oscillatory over any small set of terms. The convergence of C_n is therefore not so simply determined as is that of F_n. These properties suggest that an approximation to the $\sum_n^u$ terms in (15) can be made through removal from inside the sum of a factor F_K, where F_K is the same as F_n except that a constant frequency $\omega(K)$ is substituted for $\omega(n)$. One can interpret $\omega(K)$ as an *effective* or *average frequency* of the uncharacterized states.

Because of the sum rule (13), it is possible to write

$$\sum_n{}^u C_n = -\sum_n{}^c C_n \ . \tag{16}$$

This procedure results in a modified expression for the probability amplitude,

$$D = \frac{3}{2\omega_1\omega_2} \sum_n{}^c (F_n - F_K) C_n \ . \tag{17}$$

The value of $\omega(K)$ is often higher (more positive) than any $\omega(n)$, since states nearest the ground state are normally better characterized. If F_K is not too different from zero for a particular set u, the length form of the equations is the closest approximation to the actual amplitudes. It is in the opposite case, where $F_K \rightarrow 1$, that the limiting velocity form is superior. See below.

Since the sum rule (13) has been incorporated into (17), that equation is expected to be independent of whether the length or velocity form of the equations is used. This is easily shown to be the case, since from (9), $F_n = 1 - F_n'$ and, in addition, $F_K = 1 - F_K'$. Thus, one can equivalently write

$$D = -\frac{3}{2\omega_1\omega_2}\sum_n{}^{c}(F_n' - F_K')C_n \tag{18}$$

for D, which is (7) with an average-frequency approximation analogous to that in (17). Thus, the result D of (17) [or (18)] is independent of the gauge form chosen, even though an inexact set of intermediate states n has been employed. The gauge labels $[J_0]$ and $[J]$ have therefore been dropped. In the case of a complete set, D, $D[J_0]$, and $D[J]$ are all equivalent and exact.

Providing (15) is an accurate representation of the true amplitudes (not true for crudely approximate eigenfunctions), the exact result $D[J_0] \equiv D[J]$ can be written as a linear combination[17] of the limiting length and velocity forms, weighted by what may be thought of as an *accuracy factor* for each form:

$$D[J_0] = \alpha D^c[J_0] + (1-\alpha)D^c[J] , \tag{19}$$

where

$$\alpha = \frac{\sum_n{}^{u}(1-F_n)C_n}{\sum_n{}^{u}C_n} \approx F_K' \tag{20}$$

and $(1-\alpha) \approx F_K$. Thus, F_K' is an approximate accuracy factor for the length form. Conversely, F_K is an approximate accuracy factor for the velocity form.

VI. APPLICATION TO HYDROGEN 1s-2s TRANSITION

For the 1s-2s transition, $i = 1s$, $f = 2s$. One has (bound states)

$$C_n = \frac{1}{3}\left[\left[1 - \frac{1}{n^2} - \omega_1\right] + \left[\frac{1}{4} - \frac{1}{n^2} + \omega_1\right]\right] \times R^{n1}_{10} R^{n1}_{20} , \tag{21}$$

$$F_n = \frac{\omega_1\omega_2}{\left[1 - \frac{1}{n^2} - \omega_1\right]\left[\frac{1}{4} - \frac{1}{n^2} + \omega_1\right]} , \tag{22}$$

$$F_K = \frac{\omega_1\omega_2}{[1 + \omega(K) - \omega_1][\frac{1}{4} + \omega(K) + \omega_1]} , \tag{23}$$

where $\omega(1s) = -1$, $\omega(2s) = -\frac{1}{4}$, and $\omega(np) = -1/n^2$, where $n = 2,3,\ldots$.

Now assume hypothetically that nothing is known about states for which $n > 2$. In that case, there is only one characterized intermediate state, the $2p$ state. Required are[3]

$$R^{21}_{10} = +1.290\,27$$

and

$$R^{21}_{20} = -5.196\,15 .$$

The frequency $\omega(K)$ can be estimated by fitting the exact probability amplitude

$$D[J_0] = -11.7805$$

for $\omega_1 = 0.375$ from Table I of Ref. 1. Using this method, $\omega(K) = +0.0171$. Inserting these parameters into (21)–(23), the scattering amplitude $D[2]$ from the modified equation (17) is determined. These values are shown in Table I for various ω_1. Included also in the table are values[1] of $D[J_0]$, the exact amplitude using all discrete and continuous states, and

$$D^c[J_0] = D[J_0 2] ,$$

the amplitude obtained from the length form when only the $2p$ state is included in the "set" of intermediate states. Errors in $D[2]$ are less than 2%, while errors in $D[J_0 2]$ are 10–50% except for the three largest values of ω_1. Clearly, the modified equation (17) is much superior to the limiting $\vec{E}\cdot\vec{r}$ equation, even in the case where the entire set of bound states $n = 2, \infty$, is used in the latter equation.[1]

Extending the set of intermediate states beyond $2p$ expectedly gives better results. See Table II. Not only do the percentage errors remain about an order of magnitude less for the modified equation compared with the limiting length form, but the convergence is somewhat faster as additional states $3p$, $4p$, etc., are added.

If one starts the derivation with the $\vec{A}\cdot\vec{p}$ gauge, where $F_n' = 1 - F_n$ and $F_K' = 1 - F_K$, identical results are obtained, as mentioned earlier. This is true even though, because of the essential degeneracy of the $2s$ and $2p$ states, the $1s-2s$ probability amplitude from the limiting velocity form using the $2p$ state alone is identically zero for all ω_1. In this case, all contributions to the amplitude derive from the $F_K' C_n$ terms.

VII. OTHER AVERAGE-FREQUENCY APPROXIMATIONS

In Sec. VI, it was found that the modified equation, which is independent of the gauge form used,

TABLE I. Comparison of theoretical probability amplitudes for various ω_1 using only the $2p$ state as the "set" of intermediate states: $D[2]$ is from the modified equation (17), and $D[J_0 2]$ is from the limiting $\vec{E}\cdot\vec{r}$ equation. Compared with these results are the exact theoretical results $D[J_0]$ from Ref. 1. The percent errors relative to these exact results are given in parentheses for both $D[2]$ and $D[J_0 2]$.

ω_1	$D[J_0]$	$D[2](\%E)$	$D[J_0 2](\%E)$
0.3750	−11.7805	a	−17.8785(51.8)
0.5250	−14.7319	−14.8339(0.69)	−21.2839(44.5)
0.6750	−41.1484	−41.8616(1.73)	−49.6624(20.7)
0.6875	−49.6878	−50.5207(1.68)	−58.5113(17.8)
0.7000	−62.6595	−63.6348(1.56)	−71.8331(14.6)
0.7125	−84.5252	−85.6713(1.36)	−94.0971(11.3)
0.7250	−128.683	−130.037(1.05)	−138.712(7.79)
0.7375	−262.165	−263.772(0.61)	−272.722(4.03)
0.7475	−1334.33	−1336.18(0.14)	−1345.37(0.83)

[a] $\omega(K)$ is set equal to $+0.0171$. This causes $D[2]=D[J_0]=-11.7805$ for $\omega_1=0.3750$.

is a far better approximation of the true value of the two-photon transition amplitude than either of the two limiting forms—length or velocity—of these equations. A great advantage of the modified equation is that, except for the choice of $\omega(K)$, no additional matrix elements or parameters are required beyond those ordinarily employed when using the limiting forms, the calculation being an elementary variation on these. Use of the modified equation also eliminates the question, "which is the best gauge to use for the problem at hand?" This is equivalent to removal of an added parameter when using the conventional equations.

In spite of these advantages, it probably has already struck the reader that the comparisons made in Sec. VI are unfair. An equation containing an adjustable average-frequency term was compared with equations having no such "correction term." This criticism is partly justified. However, in choosing an alternate average-frequency approximation, one must again confront the question of gauge. If the chosen approximation violates the sum rule, it must therefore depend on the gauge form used. If this gauge form is a poor representation of the calculation being performed, then the accuracy factor α of (20) takes on some unpredictable value far removed from its acceptable limit, and errors can arise. In problems using a very limited set of intermediate states n, α may not be very close to either of its limits; neither the length nor velocity form is a particularly good approximation to the problem under consideration. Furthermore, the relative sign of an arbitrary average-frequency correction term is not always known, and additional information or

TABLE II. The values of $D[n]$ using the modified equation (17). The maximum principle quantum number used in the incomplete sum over states is n. For each n value, $\omega(K)$ has been adjusted in order to give the best fit; $D[n]=D[J_0]=-11.7805$ for $\omega_1=0.3750$. The percent errors ($\%E[J_0 n]$) in the last column are for the limiting $\vec{E}\cdot\vec{r}$ gauge and refer only to the photon energy $\omega_1=0.7000$. These should be compared with ($\%E$) for the modified equation under the 0.7000 heading in the table; percent errors are larger for smaller ω_1 and smaller for larger ω_1. In general, percent errors for the limiting $\vec{E}\cdot\vec{r}$ form are more than an order of magnitude larger than for the modified equation. Also compare with Table I, where the $n=2$ values are given.

$D[n]$ ($\%E$) \ ω_1	0.5250	0.6750	0.7000	0.7250	0.7475	$\omega(K)$	$\%E[J_0 n]$
$n=3$	−14.7735(0.28)	−41.3982(0.61)	−62.9855(0.52)	−129.111(0.33)	−1334.88(0.04)	0.126	6.44
4	−14.7608(0.20)	−41.3137(0.40)	−62.8721(0.34)	−128.957(0.21)	−1334.67(0.03)	0.174	4.78
5	−14.7561(0.16)	−41.2833(0.33)	−62.8319(0.28)	−128.904(0.17)	−1334.60(0.02)	0.198	4.14
6	−14.7537(0.15)	−41.2688(0.29)	−62.8128(0.24)	−128.879(0.15)	−1334.57(0.02)	0.212	3.83
7	−14.7524(0.14)	−41.2605(0.27)	−62.8020(0.23)	−128.865(0.14)	−1334.55(0.02)	0.221	3.64
8	−14.7515(0.13)	−41.2554(0.26)	−62.7953(0.22)	−128.856(0.13)	−1334.54(0.02)	0.227	3.52
9	−14.7509(0.13)	−41.2519(0.25)	−62.7908(0.21)	−128.850(0.13)	−1334.53(0.02)	0.232	3.45
10	−14.7505(0.13)	−41.2495(0.25)	−62.7876(0.20)	−128.846(0.13)	−1334.53(0.02)	0.235	3.39

calculations are necessary in order to determine this. In the modified equation, this question of sign is automatically taken care of by the sum rule.

To illustrate some of these points, the 1*s*-2*s* hydrogen transition will again be considered. An alternate method suggested for comparison by one of the referees of this paper is equivalent to making an average-frequency approximation on the entire $F_n C_n$ part of the $\sum_n^u$ term of (15), rather than on the frequency factor F_n alone, as was done in previous sections. After some rearrangement of terms and invoking closure, one obtains in the length form

$$\bar{D}(L)=\frac{3a_0^{-2}}{2}(1+P_{12})\left[\frac{\langle f\,|\,(\vec{e}_1\cdot\vec{r})(\vec{e}_2\cdot\vec{r})\,|\,i\,\rangle}{\omega(L)-\omega(i)-\omega_2}\right]$$

$$+(1+P_{12})\sum_n{}^c\vec{e}_1\cdot\langle f\,|\,\vec{r}\,|\,n\,\rangle\langle n\,|\,\vec{r}\,|\,i\,\rangle\cdot\vec{e}_2\left[\frac{1}{\omega(n)-\omega(i)-\omega_2}-\frac{1}{\omega(L)-\omega(i)-\omega_2}\right]. \qquad (24)$$

This average-frequency approximation, though it approaches the exact result as $\omega(L)\rightarrow\infty$, clearly violates the sum rule (13) for an inexact set. It must therefore be dependent on the gauge form chosen. In the velocity form, the equation is

$$\bar{D}(V)=-\frac{3a_0^{-2}}{2\omega_1\omega_2}[\omega(V)-\omega(f)][\omega(V)-\omega(i)](1+P_{12})\left[\frac{\langle f\,|\,(\vec{e}_1\cdot\vec{r})(\vec{e}_2\cdot\vec{r})\,|\,i\,\rangle}{\omega(V)-\omega(i)-\omega_2}\right]$$

$$+(1+P_{12})\sum_n{}^c\vec{e}_1\cdot\langle f\,|\,\vec{r}\,|\,n\,\rangle\langle n\,|\,\vec{r}\,|\,i\,\rangle\cdot\vec{e}_2\left[\frac{[\omega(n)-\omega(f)][\omega(n)-\omega(i)]}{\omega(n)-\omega(i)-\omega_2}\right.$$

$$\left.-\frac{[\omega(V)-\omega(f)][\omega(V)-\omega(i)]}{\omega(V)-\omega(i)-\omega_2}\right]. \qquad (25)$$

The "best" average frequencies $\omega(L)$ and $\omega(V)$ in the two approximations are expected to be different.

Before utilizing (24) and (25) for the 1*s*-2*s* transition, note that these equations contain matrix elements of $(\vec{e}_1\cdot\vec{r})(\vec{e}_2\cdot\vec{r})$. Their use therefore requires additional calculations or information beyond that needed in the limiting length or velocity equations or in the modified equation. For an atomic or molecular many-electron system, the accurate evaluation of such terms may be nontrivial,[16] and their presence is a distinct inconvenience. Another disadvantage is that one does not know which equation, (24) or (25), is the best. The answer to this question is not ordinarily known, and methods barely short of guess work[8] must be used to make this decision.

Table III shows the results of using (24) and (25) for the 1*s*-2*s* transition in hydrogen. The matrix element $\langle 2s\,|\,r^2\,|\,1s\,\rangle$ has the value -2.9797. Values of α have also been included in this table, in-

TABLE III. Two-photon probability amplitudes for the 1*s*-2*s* transition calculated from the average-frequency approximations (24) and (25). These values and their percent errors should be compared with those of Table I from the modified equation (17) obtained using the same fitting procedure.

ω_1	$D(L2)(\%E)$	$D(V2)(\%E)$	α
0.3750	a	a	0.659
0.5250	−14.7946(0.43)	−14.7566(0.17)	0.692
0.6750	−41.6259(1.16)	−41.2216(0.18)	0.829
0.6875	−50.2514(1.13)	−49.6776(0.02)	0.849
0.7000	−63.3271(1.07)	−62.4757(0.29)	0.872
0.7125	−85.3194(0.94)	−83.9680(0.66)	0.898
0.7250	−129.634(0.74)	−127.214(1.14)	0.928
0.7375	−263.310(0.44)	−257.519(1.77)	0.961
0.7475	−1335.66(0.10)	−1302.17(2.41)	0.992

[a] $\omega(L)$ is set equal to -0.1419 and $\omega(V)$ to $+0.0325$ to match the correct value $D[J_0]=-11.7805$ for $\omega_1=0.3750$.

dicating the superiority of length-form calculations over the range of frequencies considered. The best average frequencies, obtained by fitting to the exact amplitude at $\omega_1=0.375$ and assuming, as in Sec. VI, that the set of intermediate states consists only of the $2p$ state, are $\omega(L)=-0.1419$ and $\omega(V)=+0.0325$. The fit, being forced at $\omega_1=0.375$, causes the percent error for the results from all the equations to be abnormally small for low ω_1.

VIII. CONCLUSIONS

The results from (24) and (25), perhaps surprisingly, are of similar accuracy for the hydrogen problem even though the *limiting* length form is superior for this problem (α near unity). However, something is obviously going wrong with the velocity-form equation as resonance is approached. The modified equation (17) [or (18)] gives results that have accuracy comparable to that of the closure forms. The central point of this paper, of course, is not to improve hydrogen 1*s*-2*s* calculations, but rather to suggest a simpler, more consistent, nevertheless accurate, method of performing calculations of two-photon transition probabilities on complex atoms and molecules. It is expected that when the best gauge form to use for a specific problem is not known, or when the electronic complexity of the system leads to doubtful accuracy of r^2 or p^2 matrix elements, the use of (17) would be preferred over (24) or (25). For example, experimental oscillator strength data can be used in (17) without having to calculate or estimate these additional matrix elements.

As in all average-frequency approximations, some intuition or knowledge must be used in the application of (17). The value of $\omega(K)$ is not known *a priori*, though intelligent guesses can sometimes be made. In the H-atom problem, the $2p$ set led to an $\omega(K)$ just above the ionization limit. As further intermediate discrete states were added, $\omega(K)$ approached 0.25. See Table II. These values do not depend on gauge when using the modified equation. There may be disadvantages associated with the fact that the best average frequencies in equations like (24) and (25) are different in the two gauge forms. It must be remembered that the characterized set has to be a reasonable representation for the problem being calculated. If it contains only states whose eigenfunctions are poorly known or are otherwise inappropriate, for example, intermediate *d* states in the 1*s*-2*s* transition of hydrogen, useless results will be obtained. Questions concerning appropriate states and the value of $\omega(K)$ can sometimes be answered if a single experimental point (or exactly known theoretical point) is available, as was illustrated in the case of the 1*s*-2*s* transition. Unfortunately, few theoretical papers have traditionally reported partial two-photon amplitudes, only squared amplitudes. It is therefore impossible to use (17) to reinvestigate most existing literature transition probabilities without a full reworking of such computations.

Extension of the methods to more complex electronic systems is fairly straightforward. Take, for example, the two-photon ($\omega_1=\omega_2$) cross-section calculations of nitrogen and oxygen recently reported by Omidvar.[9] The transitions in question involve the promotion of an electron from the $2p$ orbital in the ground state to $3p$. Intermediate states are those for which $2p\rightarrow ns$ or $2p\rightarrow nd$ ($n\geq 3$). It is essential to include both types when applying the modified formalism. Taking only $n=3$ as the set, it is noted from Omidvar's paper that the *s* and *d* promotions enter $\Sigma_n^c C_n$ with the same sign for nitrogen but with the opposite sign for oxygen. Estimating the value of $\omega(K)$ to lie $0.25\mathscr{R}$ above the ionization potential, similar to the case for hydrogen, yields (units of a_0^4) cross sections for nitrogen $3.24\times10^{-2}(^4S)$, $6.94\times10^{-3}(^4D)$; and for oxygen $2.10\times10^{-4}(^3P_0)$, $6.31\times10^{-3}(^3P_2)$. Omidvar, using eight intermediate bound states ($n=3-6$) but omitting the continuum, obtained cross sections that seemed to be converging. These values were 3.49×10^{-2}, 5.07×10^{-3}, 2.18×10^{-4}, and 8.41×10^{-3}, respectively, for the above four transitions. The agreement is sufficiently good to show that no serious violation of the C_n sum rule has occurred by omitting the continuum. Nonetheless, looking at the hydrogen results, it is not valid to conclude that the continuum contribution is negligible when apparent convergence has occurred for the bound states.

In the resonance case, where ω_1 or $\omega_2\approx\omega(n)-\omega(i)$, the contributions from F_nC_n so dominate those from the nonresonant terms F_KC_n in (17) that it is immaterial whether one uses the limiting length form or the modified form of the equations. This is illustrated by the case where $\omega_1=0.7475$ for the 1*s*-2*s* transition. Furthermore, to deal with the resonance condition, damping terms $-i\Gamma(n)$ must be incorporated in the denominators in the usual manner.

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[17] It can be shown [C. W. Brown and G. W. Robinson (unpublished)] that the Lagrangian for the coupled system of field plus nonrelativistic sources can always be expressed as a weighted average of the length and velocity forms. A canonical transformation (gauge transformation of the first kind[4]) can be performed that, to an excellent approximation, takes the radiation-matter Hamiltonian to a weighted-average form. This transformation can be used to optimize transition probabilities obtained with inexact eigenfunctions. Choosing the best $\omega(K)$ in Sec. V is equivalent to choosing this optimized form. It should be noted here also that Eqs. (8) and (9), and therefore many of the relationships in this paper, depend upon the matrix identity $\vec{p}_{n'n} = -im\omega_{nn'}\vec{r}_{n'n}$, which is true only for exact eigenfunctions, or excellent approximations to them. More will be said about this aspect in a later publication.