PHYSICAL REVIEW A VOLUME 14, NUMBER 3 SEPTEMBER 1976

Multiphoton transitions: Approximations for the effective Hamiltonian*

Leonard Rosenberg
Department of Physics, New York University, New York, New York 10003

(Received 6 May 1976)

The problem of calculating transition probabilities for an atom interacting with an intense radiation field is set up within the context of an effective Hamiltonian formalism. This has the virtue that resonance effects are properly accounted for at the outset; more generally, it provides a convenient framework for approximations. Through the restriction of the class of intermediate states to be included in the construction of the effective potential, a unitary (nonperturbative) model is obtained. A successive approximation procedure for determining the effective potential, which is based on continued-fraction representations, is described. While very likely intractable for the true problem, this successive approximation procedure can be implemented, for the model effective potential, with the aid of a generalized Rayleigh-Ritz procedure described here. The level-shift matrix is constructed from the effective potential; it determines the transition probabilities, linewidths, and energy-level displacements induced by the field. We derive variational expressions of the Kohn type for each of the elements of the model level-shift matrix.

I. INTRODUCTION

The effective Hamiltonian method, widely used in scattering theory,[1] provides a convenient framework for the calculation of multiphoton transition probabilities. Resonance effects are accounted for in a simple and direct manner in this formalism through the close coupling among nearly degenerate states. The contribution of virtual, energy-nonconserving intermediate states appears in the effective potential; since the resonant states have been projected out near-singularity difficulties arising from small energy denominators are avoided, formally at least, in the calculation of the effective potential. We say "formally" since the wave functions of the atomic bound states to be projected out are in general only imprecisely known. A minimum principle, developed originally for scattering problems,[2] can be very useful in this connection since with its aid the appearance of spurious singularities can be rigorously excluded. The applicability of this minimum principle to the problem of calculating the effective potential is discussed below in Sec. IV A.

Once the effective potential matrix is determined, in some approximation, there still remains the problem of calculating the level shifts and transition amplitudes of physical interest. Here continuum effects enter, not only in the final state of the ionization process but in intermediate states as well; virtual energy-conserving transitions to continuum states give rise to the imaginary part of the level shift and must be properly accounted for. Variational methods of the Kohn type[3] can be useful in the calculation of these continuum effects, as discussed in Sec. IV B.

The calculational methods described in Sec. IV are based on a particular model of the effective Hamiltonian which is described in Sec. II. The approximation which defines the model consists, roughly speaking, of the neglect of the effect of the atom-field interaction on the propagation of the atomic system from one continuum state to another. As a consequence of this assumption the model effective Hamiltonian is Hermitian. Thus, the property that transition probabilities sum to unity can be preserved in calculations. In the limit of low photon flux the model reproduces the results of perturbation theory; it defines, then, a particular continuation of perturbation theory into the high-flux domain.[4]

In Sec. III we derive a continued-fraction representation for matrix elements of the effective potential of the model system. The structure is similar to that obtained in lowest order perturbation theory, but with intermediate-state propagators modified by the interaction of the atom with the radiation field. This is accounted for by the addition of an effective potential (or "self-energy") term to the Hamiltonian of the isolated atom. This effective potential is itself of the form given by lowest-order perturbation theory, but with a modified propagator, and so forth. The result of this analysis is the above-mentioned continued-fraction representation. The simplifying feature of the model considered here lies in the fact that these propagator modifications appear only when the energy available to the atom is insufficient to ionize it. It is for this reason that the calculational procedure described in Sec. IV could be set up in terms of commonly used bound-state and scattering techniques. Whether it will be practicable to go beyond the confines of the model in any systematic way is an interesting question, but a rather difficult one, and we shall put it aside at the present time.

II. EFFECTIVE HAMILTONIAN FORMULATION

A. Resolvent operator method

We consider the interaction of an atom with an external radiation field. The Hamiltonian is expressed as

$$H = H_A + H_F + H' , \tag{2.1}$$

where H_A is the Hamiltonian of the isolated atom. The radiation field is described in the occupation number representation. For simplicity we include only one mode, of frequency ω and linear polarization, and write for the field Hamiltonian

$$H_F = \hbar\omega a^\dagger a . \tag{2.2}$$

In the dipole approximation the photon-atom interaction takes the form

$$H' = iD(a - a^\dagger) , \tag{2.3}$$

where D is proportional to the projection of the dipole-moment operator of the atom in the direction of the polarization vector. We are concerned here with photon states of large occupation number; we therefore neglect spontaneous emission processes.

The resolvent operator[5] is defined as

$$G(E) = (E - H)^{-1} . \tag{2.4}$$

The time-evolution operator can be obtained in terms of the resolvent using the relation

$$U(t) = \frac{1}{2\pi i} \int_c dE \, e^{-iEt/\hbar} G(E) , \tag{2.5}$$

the contour c running from $+\infty$ to $-\infty$ above the real axis. We base our analysis on a partitioning technique of the type used by Feshbach[1] in the context of reaction theory. Thus, let P and $Q = 1 - P$ be projection operators, for the moment arbitrary, and consider the modified resolvent $G^Q(E)$ defined by

$$Q(H - E)QG^Q(E) = -Q . \tag{2.6}$$

Then, by straightforward algebra[6] one finds that $PG(E)P$ satisfies

$$P[H - E + HQG^Q(E)QH]PG(E)P = -P , \tag{2.7}$$

and that $G(E)$ has the representation

$$G(E) = G^Q(E) + [1 + G^Q(E)H] PG(E)P [1 + HG^Q(E)] . \tag{2.8}$$

For definiteness we shall suppose that one and only one of the bound excited states of the atom can be reached from the ground state through a resonant transition. Stated differently, the unperturbed Hamiltonian $H_0 = H_A + H_F$ is assumed to have two nearly degenerate discrete eigenstates:

$$H_0 | \alpha \rangle = \mathcal{E}_\alpha | \alpha \rangle , \quad \alpha = a, b . \tag{2.9}$$

Here $| a \rangle = | \psi_a \rangle | n_a \rangle$, with $| \psi_a \rangle$ representing the atomic ground state with eigenvalue ϵ_a while n_a gives the photon number; we have $\mathcal{E}_a = \epsilon_a + n_a \hbar\omega$. The state $| b \rangle = | \psi_b \rangle | n_b \rangle$ is similarly defined. We take as our projection operator

$$P = | a \rangle \langle a | + | b \rangle \langle b | + | n_c \rangle \langle n_c | . \tag{2.10}$$

Here we have singled out the photon state $| n_c \rangle$ which is reached after the atom, originally in its ground state, has absorbed the *minimum* number of photons necessary to raise its energy above the continuum threshold. At this stage the atom is in a continuum state with energy $\mathcal{E}_a - n_c \hbar\omega$. The wave function of this state must ultimately be constructed (see Sec. IV B) but it will be convenient not to introduce that function explicitly at this point. We therefore deal with an effective Hamiltonian which is an operator with respect to continuum states.

We introduce the 3×3 matrix

$$[\underline{G}(E)]_{\mu\nu} \equiv \langle \mu | G(E) | \nu \rangle , \quad \mu, \nu = a, b, n_c . \tag{2.11}$$

Equation (2.7) is equivalent to

$$PGP = G_0^P + G_0^P \, VPGP , \tag{2.12}$$

where we have defined the unperturbed resolvent

$$G_0^P(E) = [P(E - H_0)P]^{-1} \tag{2.13}$$

and the effective potential

$$V(E) = H' + H' G^Q(E) H' . \tag{2.14}$$

The matrix version of Eq. (2.12) can be expressed as

$$\underline{G}^{-1} = \underline{G}_0^{-1} - \underline{V} \equiv E \underline{1} - \underline{H}_{\text{eff}} , \tag{2.15}$$

where $\underline{1}$ is the 3×3 unit matrix and the effective Hamiltonian matrix is given by

$$[\underline{H}_{\text{eff}}]_{\mu\nu} = \langle \mu | H_0 + V | \nu \rangle , \quad \mu, \nu = a, b, n_c . \tag{2.16}$$

To facilitate the construction of $\underline{G}$ through the inversion of $E\underline{1} - \underline{H}_{\text{eff}}$ we make use of the identity, Eq. (2.8), suitably reinterpreted so that it applies to the matrix $\underline{G}$ rather than to the full resolvent, with P replaced by $\underline{P}_d$; $[\underline{P}_d]_{\mu\nu} = \delta_{\mu\nu} - \delta_{\mu n_c} \delta_{\nu n_c}$. We find that in the space of the discrete states

$$G_{\alpha\beta} = [\underline{G}_d]_{\alpha\beta} , \quad \alpha, \beta = a, b , \tag{2.17}$$

with

$$\underline{G}_d = [\underline{P}_d (E\underline{1} - \underline{H}_0 - \underline{R}) \underline{P}_d]^{-1} . \tag{2.18}$$

The level-shift matrix is here defined by

$$R_{\mu\nu} = V_{\mu\nu} + V_{\mu n_c} (E - H_A - n_c \hbar\omega - V_{n_c n_c})^{-1} V_{n_c \nu} , \tag{2.19}$$

for $\mu,\nu=a,b,n_c$. Inversion of the 2×2 matrix appearing in Eq. (2.18) can be carried out explicitly; the elements are numbers, not operators. One finds

$$G_{ba}=R_{ba}[(E-\mathcal{E}_b-R_{bb})(E-\mathcal{E}_a-R_{aa})-R_{ba}R_{ab}]^{-1}, \tag{2.20a}$$

$$G_{aa}=(E-\mathcal{E}_b-R_{bb})[(E-\mathcal{E}_b-R_{bb})(E-\mathcal{E}_a-R_{aa})-R_{ba}R_{ab}]^{-1}, \tag{2.20b}$$

with the remaining two elements obtained by interchange of indices a and b in Eqs. (2.20). Once $\underline{G}_d$ has been constructed the remaining elements of $\underline{G}$ are determined by the relations ($\alpha,\beta=a,b$)

$$G_{n_c\beta}=\sum_{\gamma=a,b}(E-H_A-n_c\hbar\omega-V_{n_cn_c})^{-1}V_{n_c\gamma}G_{\gamma\beta}, \tag{2.21a}$$

$$G_{\alpha n_c}=\sum_{\gamma=a,b}G_{\alpha\gamma}V_{\gamma n_c}(E-H_A-n_c\hbar\omega-V_{n_cn_c})^{-1}, \tag{2.21b}$$

$$G_{n_cn_c}=(E-H_A-n_c\hbar\omega-V_{n_cn_c})^{-1}+\sum_{\gamma=a,b}\sum_{\delta=a,b}(E-H_A-n_c\hbar\omega-V_{n_cn_c})^{-1}\times V_{n_c\gamma}G_{\gamma\delta}V_{\delta n_c}\times(E-H_A-n_c\hbar\omega-V_{n_cn_c})^{-1}. \tag{2.21c}$$

If the final state of interest has the photon number $m<n_c$ the relevant matrix element can be seen from Eq. (2.8) to be

$$\langle m|G|\mu\rangle=\langle m|G^QH'PGP|\mu\rangle,\quad \mu=a,b,n_c. \tag{2.22}$$

This may be shown without much difficulty to be expressible in the alternative form

$$\langle m|G|\mu\rangle=(E-H_A-m\hbar\omega)^{-1}V_{mn_c}G_{n_c\mu}. \tag{2.23}$$

We see that all the matrix elements of interest can be expressed in terms of the effective potential V. The bare interaction H' no longer appears explicitly. The problem has now been shifted to the calculation of the effective potential.

B. Unitary model

We have, in Sec. II A, an exact reformulation of the original problem in which three degenerate states (the two discrete states a and b and the continuum state with n_c photons in the field) are explicitly accounted for in the effective Hamiltonian. There are of course other states degenerate with these three. These additional states correspond to photon number $m<n_c$; for m small enough the residual ion may be left with enough energy to excite it, or break it up. The presence of these additional states is implicit in the effective potential. We now set up an approximation scheme in which the possibility of real or virtual transitions to such states is ignored. This corresponds to replacing the exact effective potential V by a model potential $\hat{V}$ characterized by the property

$$\hat{V}_{n_cn_c}=0. \tag{2.24}$$

As a further simplification we ignore the variation of the effective potential with respect to the energy parameter [see Eq. (2.14)]; we take $\hat{V}=\hat{V}(\mathcal{E})$ with $\mathcal{E}=\mathcal{E}_a$. To see that these assumptions exclude the appearance of energy-conserving intermediate states in the expansion of the effective-potential matrix $\underline{\hat{V}}$ consider first the element $\hat{V}_{n_ca}$. The only states with energy $\mathcal{E}$ which have not been projected out are those with photon number $m<n_c$. To reach such a state starting with $|n_a\rangle$ it is necessary to pass through state $|n_c\rangle$ since each interaction changes the photon number by one unit; but $|n_c\rangle$ has been projected out. A similar argument holds for the remaining elements of $\underline{\hat{V}}$. It does not hold, evidently, if the photon number is n_c in both initial and final states, but $\hat{V}_{n_cn_c}=0$ in the model.

The fact that there are no vanishing energy denominators (in other words, that the Green's functions from which $\underline{\hat{V}}$ is constructed are nonsingular) implies that $\underline{\hat{V}}$ is Hermitian. The same property holds for $\underline{\hat{H}}_{\text{eff}}$ in the space of square-integrable functions. This guarantees the unitarity property of the time-evolution operator

$$\underline{\hat{U}}=\frac{1}{2\pi i}\int_c dE\,e^{-iEt/\hbar}\,\underline{\hat{G}}(E); \tag{2.25}$$

the proof, based on the Schrödinger equation

$$\left(i\hbar\frac{\partial}{\partial t}-\underline{\hat{H}}_{\text{eff}}\right)\underline{\hat{U}}(t)=0, \tag{2.26}$$

is standard.[7] We are then assured that the sum of the transition probabilities over the three allowed final states will give unity.

The level-shift matrix $\underline{\hat{R}}$ is obtained from Eq. (2.19) with $\underline{V}$ replaced by $\underline{\hat{V}}$. Specifically we have $\hat{R}_{n_cn_c}=0$, $\hat{R}_{n_c\beta}=\hat{V}_{n_c\beta}$, $\hat{R}_{\alpha n_c}=\hat{V}_{\alpha n_c}$, and

$$\hat{R}_{\alpha\beta}=\hat{V}_{\alpha\beta}+\hat{V}_{\alpha n_c}(E-H_A-n_c\hbar\omega)^{-1}\hat{V}_{n_c\beta}, \tag{2.27}$$

with $\alpha,\beta=a,b$. The problem of determining approximations for the model potential $\underline{\hat{V}}$ and the associated level shift $\underline{\hat{R}}$ is discussed in Secs. III and IV. Once this is accomplished, and $\underline{\hat{G}}$ constructed, transition probabilities can be found using Eq. (2.25). The contour integration is easily performed if, as we shall assume, the energy dependence of $\hat{R}_{\alpha\beta}$ is simplified by the replacement of E with $\mathcal{E}$ in Eq. (2.27).[8] In this way one obtains explicit expressions for the transition probabilities in terms of the elements of the level-shift matrix $\underline{\hat{R}}(\mathcal{E})$. Similar expressions have been given previously[6,9] and we shall not repeat the derivation here. Rather, we turn immediately to the calculational problem, now well defined, of determining the matrix $\underline{\hat{R}}(\mathcal{E})$.

III. CONTINUED-FRACTION REPRESENTATIONS

The use of continued fractions for the evaluation of transition probabilities has a long history which we shall not attempt to review here. Some recent work along these lines can be found in Ref. 4. Here we derive continued-fraction representations for elements of the effective potential matrix $\underline{\hat{V}}$ introduced in Sec. II B. They reduce, in the appropriate limit, to the representations derived previously for a two-level atom.[10] In Sec. IV A we discuss a variational method of the Rayleigh-Ritz type for evaluating the effective potential in its continued-fraction form.

Our procedure is based on successive applications of the partitioning identity, Eq. (2.8); in each such application a particular photon state is projected out. Consider first one of the diagonal elements $\hat{V}_{\alpha\alpha}$, $\alpha = a, b$. We write

$$\hat{V}_{\alpha\alpha} = \langle \psi_\alpha | \mathcal{V}_{\alpha\alpha} | \psi_\alpha \rangle , \tag{3.1}$$

with

$$\mathcal{V}_{\alpha\alpha} = \langle n_\alpha | \hat{V} | n_\alpha \rangle . \tag{3.2}$$

To simplify the notation we shall, throughout the remainder of this section, write n and $\mathcal{V}$ rather than n_α and $\mathcal{V}_{\alpha\alpha}$. We begin by projecting out the state $|n\rangle$ from the Green's function which appears in the definition of the effective potential [see Eq. (2.14)]. Using the appropriate version of Eq. (2.8) we obtain the relation

$$\mathcal{V} = \mathcal{V}_n + \mathcal{V}_n q (\mathcal{E} - H_A - n\hbar\omega - \mathcal{V}_n)^{-1} q \mathcal{V}_n . \tag{3.3}$$

The projection operator $q = 1 - |\psi_\alpha\rangle\langle\psi_\alpha|$ appears since the state $|\psi_\alpha\rangle |n\rangle$ must be excluded. (In the following, for simplicity, the required atomic-state projectors will be implied rather than explicitly indicated.) Equation (3.3) has a simple interpretation. $\mathcal{V}_n$ represents the sum of all those terms in the perturbation expansion of $\mathcal{V}$ in which the photon state $|n\rangle$ never appears as an intermediate state. If we write

$$\begin{aligned}(\mathcal{E} - H_A - n\hbar\omega - \mathcal{V}_n)^{-1} &= (\mathcal{E} - H_A - n\hbar\omega)^{-1} \\ &\quad + (\mathcal{E} - H_A - n\hbar\omega)^{-1} \mathcal{V}_n (\mathcal{E} - H_A - n\hbar\omega)^{-1} + \cdots ,\end{aligned} \tag{3.4}$$

it becomes clear that the second term on the right-hand side of Eq. (3.3) represents the terms in which $|n\rangle$ appears once as an intermediate state, plus those in which it appears twice, and so forth. This Dyson-type perturbative analysis will be used repeatedly in the following for the sake of clarity. The validity of the results does not depend on the convergence of the perturbation expansion; it is a simple matter to verify the results algebraically using Eq. (2.8).

To continue we write

$$\mathcal{V}_n = \mathcal{V}_{n+} + \mathcal{V}_{n-} . \tag{3.5}$$

Here $\mathcal{V}_{n+}$ contains intermediate states with photon number greater than n; the remaining states with photon number less than n contribute to $\mathcal{V}_{n-}$. Consider first $\mathcal{V}_{n+}$. The perturbation terms can be classified according to the number of times the state $|n+1\rangle$ appears in the sum over states. Thus, the second-order contribution is

$$D \frac{n+1}{\mathcal{E} - H_A - (n+1)\hbar\omega} D . \tag{3.6}$$

This term describes the emission of a photon, the free propagation of the atom in the presence of $n+1$ photons, followed by the absorption of a photon. Higher-order terms repeat the initial emission and final absorption processes and introduce propagator modifications. The latter represent virtual transitions, starting with the state $|n+1\rangle$, to states of higher occupation number and then back down to the state $|n+1\rangle$. Let $\mathcal{V}_{(n+1)+}$ represent the sum of all such terms in which $|n+1\rangle$ does not appear as an *intermediate* state. Then, in analogy with the interpretation placed on Eq. (3.3), we may conclude that $\mathcal{V}_{n+}$ has the representation

$$\mathcal{V}_{n+} = D \frac{n+1}{\mathcal{E} - H_A - (n+1)\hbar\omega - \mathcal{V}_{(n+1)+}} D . \tag{3.7}$$

A similar analysis of the effective-potential operator $\mathcal{V}_{(n+1)+}$ leads to the representation

$$\mathcal{V}_{(n+1)+} = D \frac{n+2}{\mathcal{E} - H_A - (n+2)\hbar\omega - \mathcal{V}_{(n+2)+}} D , \tag{3.8}$$

where $\mathcal{V}_{(n+2)+}$ is the effective-potential operator associated with the state $|n+2\rangle$. The obvious extension of this procedure provides a continued-fraction representation of $\mathcal{V}_{n+}$. Application of a similar analysis to $\mathcal{V}_{n-}$ leads to

$$\mathcal{V}_{n-} = D \frac{n-1}{\mathcal{E} - H_A - (n-1)\hbar\omega - \mathcal{V}_{(n-1)-}} D , \tag{3.9}$$

and so forth. In this case, however, the sequence terminates; $\mathcal{V}_{(n_c+1)-}$ vanishes since the state $|n_c\rangle$ has been projected out.

We continue with a similar analysis of the off-diagonal elements of $\hat{V}$. We first look at elements of the form $\langle m | \hat{V} | n \rangle$, with $m < n$. The cases of interest are (i) $m = n_b$, $n = n_a$; (ii) $m = n_c$, $n = n_a$ or n_b. Here again we begin, for the sake of orientation, with the lowest-order perturbation contribution which is[11]

$$i^{(n-m)} \left(\frac{n!}{m!}\right)^{1/2} D[\mathcal{E} - H_A - (m+1)\hbar\omega]^{-1} D \cdots \times [\mathcal{E} - H_A - (n-1)\hbar\omega]^{-1} D . \tag{3.10}$$

In considering the form of the correction terms we note firstly that the initial photon state $|n\rangle$ may reappear as an intermediate state. The sum of all such terms may be put in the form of the initial-state correction factor

$$1 + (\mathcal{E} - H_A - n\hbar\omega)^{-1}\mathcal{V}_n + (\mathcal{E} - H_A - n\hbar\omega)^{-1}\mathcal{V}_n(\mathcal{E} - H_A - n\hbar\omega)\mathcal{V}_n + \cdots = 1 + (\mathcal{E} - H_A - n\hbar\omega - \mathcal{V}_n)^{-1}\mathcal{V}_n . \tag{3.11}$$

We now include corrections to the intermediate-state propagators. The correct prescription requires the replacement

$$(\mathcal{E} - H_A - p\hbar\omega)^{-1} \to (\mathcal{E} - H_A - p\hbar\omega - \mathcal{V}_{p-})^{-1} , \tag{3.12}$$

for $p = n-1, \ldots, m+1$. In checking this we start with $p = n-1$ and apply the same type of reasoning that led to Eqs. (3.7) and (3.8). [We have $\mathcal{V}_{(n-1)-}$ in the modified propagator (rather than, say, $\mathcal{V}_{(n-1)}$) since all virtual transitions to photon state $|n\rangle$ have already been included in the initial-state correction factor, Eq. (3.11), and we must avoid double counting.] The propagator modifications for $p = n-2, \ldots, m+1$ are then introduced successively in a similar way.

The remaining class of correction terms account for virtual transitions from the final photon state $|m\rangle$ to states with photon number less than m and then back to $|m\rangle$. These may be summed in the form of a final-state correction factor

$$1 + \mathcal{V}_{m-}(\mathcal{E} - H_A - m\hbar\omega - \mathcal{V}_{m-})^{-1} . \tag{3.13}$$

Putting all the correction factors together we have

$$\langle m | \hat{V} | n \rangle = i^{(m-n)} \left(\frac{n!}{m!}\right)^{1/2} [1 + \mathcal{V}_{m-}(\mathcal{E} - H_A - m\hbar\omega - \mathcal{V}_{m-})^{-1}] D [\mathcal{E} - H_A - (m+1)\hbar\omega - \mathcal{V}_{(m+1)-}]^{-1} D \cdots \times [\mathcal{E} - H_A - (n-1)\hbar\omega - \mathcal{V}_{(n-1)-}]^{-1} D [1 + (\mathcal{E} - H_A - n\hbar\omega - \mathcal{V}_n)^{-1}\mathcal{V}_n] . \tag{3.14}$$

For $m = n_c$ we would make use of the relation $\mathcal{V}_{(n_c+1)-} = 0$ which was noted above. We also have $\mathcal{V}_{n_c-} = 0$ by virtue of the basic assumption of the model, namely, $\langle n_c | \hat{V} | n_c \rangle = 0$.

The remaining elements of $\hat{V}$ are obtained using the Hermiticity relation

$$\langle \mu | \hat{V} | \nu \rangle = \langle \nu | \hat{V} | \mu \rangle^* . \tag{3.15}$$

This completes the construction of $\hat{V}$ in terms of "dressed" propagators and "dressed" initial and final states.[12] Each of the effective-potential operators which appear here have continued-fraction representations of the type discussed above in connection with Eqs. (3.7) and (3.9).

IV. VARIATIONAL APPROXIMATIONS

A. Minimum principle for the effective potential

The nonsingular nature of the Green's functions which appear in the definition of $\hat{V}$ suggests the use of a minimum principle as an approximation procedure. To describe this procedure in its simplest context we consider the expression (3.6) for the second-order contribution to $\mathcal{V}_{n+}$. As in a Rayleigh-Ritz bound-state calculation we suppose that the atomic Hamiltonian H_A has been diagonalized in a finite orthonormal basis $\{\phi_i\}$, $i = 1, 2, \ldots, N$. Corresponding to this matrix representation of H_A we have the approximate Green's function

$$(\epsilon - H_A)^{-1} \cong \sum_{i=1}^{N} | \phi_i \rangle (\langle \phi_i | \epsilon - H_A | \phi_i \rangle)^{-1} \langle \phi_i | . \tag{4.1}$$

Here $\epsilon = \mathcal{E} - (n+1)\hbar\omega$ or, since $\mathcal{E} = \epsilon_a + n_a\hbar\omega$, we have, for $n = n_a$ or n_b,

$$\epsilon = \epsilon_a + (n_a - n - 1)\hbar\omega . \tag{4.2}$$

For $n = n_a$, ϵ lies below the ground-state level ϵ_a.

In this case the variational approximation, Eq. (4.1), is known to provide a minimum principle for diagonal matrix elements of the Green's function.[13] This allows for systematic improvements through the optimization of the choice of basis functions ϕ_i. The minimum principle can be thought of as a generalization of the Rayleigh-Ritz minimum principle for the ground-state energy. Now with $n = n_b$ in Eq. (4.2) we see that $\epsilon > \epsilon_a$ for $n_a - n_b - 1 > 0$. We consider the possibility of a finite number, say M, of energy levels lying below ϵ. Even when the eigenfunctions associated with eigenvalues ϵ_i, $i = 1, 2, \ldots M$ (we adopt the ordering $\epsilon_i \leqslant \epsilon_{i+1}$ with $\epsilon_1 = \epsilon_a$) are imprecisely known the minimum principle is preserved provided that $N \geqslant M$ and the functions $\phi_1, \phi_2, \ldots, \phi_M$ are sufficiently accurate approximations to the corresponding eigenfunctions to give binding-energy estimates which all lie below ϵ.[2] The functions ϕ_i, $i > M$, can be thought of as pseudostates representing, in a variational sense, the effect of the remainder of the spectrum of H_A.

If $n = n_b = n_a - 1$ in Eq. (4.2), we have $\epsilon = \epsilon_a$. The expression (3.6) is of course nonsingular since the state $|\psi_a\rangle$ is to be projected out. We now see how this projection is to be accomplished in practice when, as is usually the case, the ground-state wave function is imprecisely known; we simply omit the term $i = 1$ in the sum in Eq. (4.1). The existence of the minimum principle guarantees that spurious singularities associated with vanishing energy denominators are rigorously avoided. (These difficulties are trivially avoided if, as often happens in lowest-order perturbation calculations, the trial function can be made orthogonal to the bound-state function to be projected out by making use of simple symmetry considerations, such as parity. In the multiphoton case we are not dealing with lowest-order perturbation theory and this simple resolution of the problem is not generally available. A detailed discussion of these near singularity difficulties, and the use of minimum principles to circumvent them, is contained in Ref. 14.)

The above discussion of the variational construction of the second-order term, Eq. (3.6), can be extended directly to higher-order terms in the perturbation expansion. In fact, the variational approach can be useful in computations based on the nonperturbative continued-fraction procedure described in Sec. III. The simplifying feature is the separable nature of the approximate Green's function, Eq. (4.1). Consider, for example, the continued-fraction expansion of $\mathcal{V}_{n+}$, $n = n_a$ or n_b. In practice we must truncate; suppose we have done so by setting $\mathcal{V}_{(n+p+1)+} = 0$. Then, with the form (4.1) used as an approximation to the unperturbed atomic Green's function we have

$$\mathcal{V}_{(n+p)+} \cong D \sum_{i=1}^{N} |\phi_i\rangle \frac{n+p+1}{\langle\phi_i|\epsilon - H_A|\phi_i\rangle} \langle\phi_i| D , \tag{4.3}$$

with $\epsilon = \mathcal{E} - (n+p+1)\hbar\omega$. The next step in the calculational procedure is the evaluation of

$$\mathcal{V}_{(n+p-1)+} = D \frac{n+p}{\mathcal{E} - H_A - (n+p)\hbar\omega - \mathcal{V}_{(n+p)+}} D . \tag{4.4}$$

The propagator in Eq. (4.4) is of the form

$$\frac{1}{x-y} = \frac{1}{x} + \frac{1}{x} y \frac{1}{x-y} , \tag{4.5}$$

with $x = \mathcal{E} - H_A - (n+p)\hbar\omega$ and $y = \mathcal{V}_{(n+p)+}$ given by Eq. (4.3). The solution to Eq. (4.5) is obtained by algebra since $1/x$ is of finite rank.[15] This procedure can be continued, leading to an approximation for $\mathcal{V}_{n+}$.

The same method is applicable to the evaluation of the continued-fraction form for the operators $\mathcal{V}_{m-}$, $n_c + 2 \leqslant m \leqslant n_a$, which are required for the construction of the effective-potential matrix $\underline{\hat{V}}$. In these cases the truncation is accomplished by setting $\mathcal{V}_{(n_c+1)-} = 0$; this is not an additional approximation, but is a consequence of the definition of $\underline{\hat{V}}$.

B. Variational principles for level shifts

It will be convenient, as in Eqs. (3.1) and (3.2), to express the effective potential in terms of matrix elements of an operator taken with respect to atomic wave functions. Thus, we define, for $\alpha, \beta = a, b$,

$$\mathcal{V}_{\alpha\beta} = \langle n_\alpha | \hat{V} | n_\beta \rangle , \tag{4.6a}$$

$$\mathcal{V}_{\alpha c} = \langle n_\alpha | \hat{V} | n_c \rangle , \tag{4.6b}$$

$$\mathcal{V}_{c\beta} = \langle n_c | \hat{V} | n_\beta \rangle . \tag{4.6c}$$

Here we assume that these amplitudes are known in some approximation, e.g., one of the approximations discussed in Sec. III. There still remains the task of constructing the level-shift matrix. In the model defined in Sec. II the "bound-bound" elements corresponding to the discrete states a and b are given by Eq. (2.27) which we write

$$\hat{R}_{\alpha\beta} = (\psi_\alpha, \mathcal{V}_{\alpha\beta}\psi_\beta) + (\psi_\alpha, \mathcal{V}_{\alpha c}[\epsilon - H_A]^{-1}\mathcal{V}_{c\beta}\psi_\beta) . \tag{4.7}$$

Here we have fixed the energy parameter E at the value $\mathcal{E}$,[8] and have defined $\epsilon = \mathcal{E} - n_c\hbar\omega$; this energy lies above the ionization threshold of the atom. The "bound-free" element is

$$(\psi_{\vec{k}}^{(-)}, \mathcal{V}_{c\beta}\psi_\beta) \equiv T_\beta^{(+)}(\hat{k})\,. \tag{4.8}$$

The continuum function $\psi_{\vec{k}}^{(-)}$ satisfies

$$(H_A - \epsilon)\,\psi_{\vec{k}}^{(-)} = 0 \tag{4.9}$$

and incoming-wave boundary conditions. We now introduce some notation which allows us to express these boundary conditions in explicit form.

The atom, assumed to be neutral, has atomic number Z. We consider the region of configuration space where one of the electrons, say electron 1, is far from the ion and carries off the energy

$$(\hbar^2/2m)\,k^2 = \epsilon - \epsilon_I\,; \tag{4.10}$$

ϵ_I represents the ground-state energy of the residual ion. (We assume that the available energy ϵ is insufficient to allow ion excitation.) The normalized, antisymmetrized ground-state wave function of the ion is $B(\vec{y})$, where $\vec{y} \equiv (2, 3, \ldots, Z)$ represents the space and spin coordinates of the ion. To avoid technical complications associated with angular momentum coupling we assume that the ion has zero total spin and zero total orbital angular momentum. Spin-dependent forces will be ignored. In order to describe the motion of the electron with spatial coordinate $\vec{r}_1 \equiv \vec{x}$ in the Coulomb field of the positive ion we make use of the modified plane wave[16]

$$u^{(\pm)}(\vec{k}, \vec{x}) = \sum_{l=0}^{\infty} \frac{(2l+1)\, i^l P_l(\hat{k}\cdot\hat{x})\, e^{\pm i\sigma_l} F_l(kx)}{kx}\,. \tag{4.11}$$

The radial function F_l has the asymptotic form

$$F_l(kx) \sim \sin(kx - \gamma \ln 2kx - \tfrac{1}{2} l\pi + \sigma_l), \quad x \to \infty\,, \tag{4.12}$$

with

$$\gamma = me^2/\hbar^2 k\,, \tag{4.13}$$

$$\sigma_l = \arg\Gamma(l + 1 + i\gamma)\,. \tag{4.14}$$

The asymptotic form of the wave function $\psi_{\vec{k}}^{(\pm)}$ in the region $x \to \infty$, corresponding to outgoing-wave (+) or incoming-wave (−) boundary conditions, may now be expressed as

$$\begin{aligned} \psi_{\vec{k}}^{(\pm)} \sim Z^{-1/2} B(\vec{y})\,\chi(1)\{&(2\pi)^{-3/2} u^{(\pm)}(\vec{k}, \vec{x}) \\ &+ C\,T^{(\pm)}(\pm\hat{x}\cdot\hat{k}) \\ &\times \exp[\pm i(kx - \gamma \ln 2kx)]/x\}\,. \end{aligned} \tag{4.15}$$

Here $\chi(1)$ is the spin function of electron 1 and C is a normalization constant which is chosen for later convenience as

$$C = -(2m/\hbar^2)\,[(2\pi)^{3/2}/4\pi]\,. \tag{4.16}$$

The physical elastic scattering amplitude is $T^{(+)}(\hat{k}\cdot\hat{k}')$, where $\hat{k}'$ and $\hat{k}$ are the directions of the initial and final momentum vectors, respectively. The Kohn variational principle[3] provides a useful calculational procedure for determining the scattering amplitude. The basis for the Kohn principle may be taken to be the identity

$$T^{(+)}(\hat{k}\cdot\hat{k}') = T_t^{(+)}(\hat{k}\cdot\hat{k}') + (\psi_{\vec{k}}^{(-)}, [H_A - \epsilon]\,\psi_{\vec{k}'t}^{(+)}) \tag{4.17}$$

which, in its partial wave form, was given by Kato.[17] The trial function has the same asymptotic form as the exact function $\psi_{\vec{k}}^{(+)}$ but with $T^{(+)}(\hat{x}\cdot\hat{k}')$ replaced by the trial amplitude $T_t^{(+)}(\hat{x}\cdot\hat{k}')$. The variational expression for $T^{(+)}$ is obtained from the identity (4.17) by replacing $\psi_{\vec{k}}^{(-)}$ on the right-hand side with $\psi_{\vec{k}t}^{(-)}$. The error thus incurred is of second order, i.e., it is bilinear in the error functions $\psi_{\vec{k}'}^{(+)} - \psi_{\vec{k}'t}^{(+)}$ and $\psi_{\vec{k}}^{(-)} - \psi_{\vec{k}t}^{(-)}$.

The identity, Eq. (4.17), may be derived by evaluating

$$J_{\vec{k}\vec{k}'} \equiv (\psi_{\vec{k}}^{(-)}, [H_A - \epsilon]\,\psi_{\vec{k}'t}^{(+)}) - (\psi_{\vec{k}'t}^{(+)}, [H_A - \epsilon]\,\psi_{\vec{k}}^{(-)})^* \tag{4.18}$$

in two ways. Firstly, we have

$$J_{\vec{k}\vec{k}'} = (\psi_{\vec{k}}^{(-)}, [H_A - \epsilon]\,\psi_{\vec{k}'t}^{(+)})\,, \tag{4.19}$$

since $\psi_{\vec{k}}^{(-)}$ satisfies the Schrödinger equation. Secondly, one may make use of Green's theorem. The surface term can be evaluated using the known asymptotic form of the wave functions. This part of the calculation is carried through most readily with the help of partial wave expansions of the incident and scattered waves describing the relative electron-ion motion in the asymptotic domain; we omit the details here.

A similar variational procedure can be set up for the calculation of the level-shift matrix elements defined in Eqs. (4.7) and (4.8). Thus, Eq. (4.7) may be expressed in the alternative forms

$$\hat{R}_{\alpha\beta} = (\psi_\alpha, \mathcal{V}_{\alpha\beta}\psi_\beta) + (\psi_\alpha, \mathcal{V}_{\alpha c} L_\beta^{(+)})\,, \tag{4.20a}$$

$$\hat{R}_{\alpha\beta} = (\psi_\alpha, \mathcal{V}_{\alpha\beta}\psi_\beta) + (L_\alpha^{(-)}, \mathcal{V}_{c\beta}\psi_\beta)\,. \tag{4.20b}$$

The functions $L_\beta^{(\pm)}$, $\beta = a, b$, are defined by the differential equation

$$(H_A - \epsilon)\, L_\beta^{(\pm)} = -\mathcal{V}_{c\beta}\psi_\beta \tag{4.21}$$

and the boundary condition

$$\begin{aligned} L_\beta^{(\pm)} \sim Z^{-1/2} B(\vec{y})\,\chi(1)\, C\, T_\beta^{(\pm)}(\pm\hat{x}) \\ \times \exp[\pm i(kx - \gamma \ln 2kx)]/x\,, \end{aligned} \tag{4.22}$$

valid for $x \to \infty$. Our notation anticipates the fact, proved below, that the amplitude $T_\beta^{(+)}$ in Eq. (4.22) can be identified with the "bound-free" level-shift matrix element defined in Eq. (4.8). To derive a variational expression for $\hat{R}_{\alpha\beta}$ we proceed, in analogy with the derivation of Eq. (4.17), by considering the expression

$$J_{\alpha\beta} \equiv (L_\alpha^{(-)}, [H_A - \epsilon] L_{\beta t}^{(+)}) - (L_{\beta t}^{(+)}, [H_A - \epsilon] L_\alpha^{(-)})^* , \tag{4.23}$$

where $L_{\beta t}^{(+)}$ is a trial function whose asymptotic behavior is given by Eq. (4.22) with $T_\beta^{(+)}$ replaced by $T_{\beta t}^{(+)}$. Use of Green's theorem, and the observation that the surface term vanishes, allows us to conclude that $J_{\alpha\beta} = 0$. This relation, along with the differential equation satisfied by $L_\alpha^{(-)}$, implies that

$$(L_\alpha^{(-)}, [H_A - \epsilon] L_{\beta t}^{(+)}) + (L_{\beta t}^{(+)}, \mathcal{V}_{c\alpha} \psi_\alpha)^* = 0 . \tag{4.24}$$

From the Hermiticity property of the level shift we have

$$(L_{\beta t}^{(+)}, \mathcal{V}_{c\alpha} \psi_\alpha)^* = (\psi_\alpha, \mathcal{V}_{\alpha c} L_{\beta t}^{(+)}) . \tag{4.25}$$

Then, by adding Eqs. (4.20b) and (4.24) and taking into account Eq. (4.25) we obtain the identity

$$\begin{aligned}\hat{R}_{\alpha\beta} = &(L_\alpha^{(-)}, [(H_A - \epsilon) L_{\beta t}^{(+)} + \mathcal{V}_{c\beta} \psi_\beta])\\ &+ (\psi_\alpha, \mathcal{V}_{\alpha\beta} \psi_\beta) + (\psi_\alpha, \mathcal{V}_{\alpha c} L_{\beta t}^{(+)}) .\end{aligned} \tag{4.26}$$

The replacement of $L_\alpha^{(-)}$ by a trial function $L_{\alpha t}^{(-)}$ leads to an error of second order since $L_\alpha^{(-)}$ appears in Eq. (4.26) in an integral which is itself a first-order quantity.

We proceed in a similar way to obtain a variational expression for the bound-free level-shift matrix element. Thus, we consider

$$J_{\vec{k}\beta} \equiv (\psi_{\vec{k}}^{(-)}, [H_A - \epsilon] L_{\beta t}^{(+)}) - (L_{\beta t}^{(+)}, [H_A - \epsilon] \psi_{\vec{k}}^{(-)})^* . \tag{4.27}$$

The second term on the right-hand side vanishes by virtue of Eq. (4.9). Use of Green's theorem leads, after evaluation of the surface term, to

$$J_{\vec{k}\beta} = - T_{\beta t}^{(+)} (\hat{k}) . \tag{4.28}$$

We then have the relation

$$\begin{aligned}-T_{\beta t}^{(+)} (\hat{k}) &= (\psi_{\vec{k}}^{(-)}, [H_A - \epsilon] L_{\beta t}^{(+)})\\ &= (\psi_{\vec{k}}^{(-)}, [(H_A - \epsilon) L_{\beta t}^{(+)} + \mathcal{V}_{c\beta} \psi_\beta])\\ &\quad - (\psi_{\vec{k}}^{(-)}, \mathcal{V}_{c\beta} \psi_\beta) .\end{aligned} \tag{4.29}$$

Consider the particular choice $L_{\beta t}^{(+)} = L_\beta^{(+)}$. It follows that $T_{\beta t}^{(+)} = T_\beta^{(+)}$. By making use of Eq. (4.21) we then see that Eq. (4.29) reduces to

$$T_\beta^{(+)} (\hat{k}) = (\psi_{\vec{k}}^{(-)}, \mathcal{V}_{c\beta} \psi_\beta) . \tag{4.30}$$

Since this relation coincides with Eq. (4.8), it confirms the identification we have made of the amplitude of the outgoing wave in Eq. (4.22) with the bound-free level-shift matrix element. The second version of Eq. (4.29) may now be written

$$T_\beta^{(+)} (\hat{k}) = T_{\beta t}^{(+)} (\hat{k}) + (\psi_{\vec{k}}^{(-)}, [(H_A - \epsilon) L_{\beta t}^{(+)} + \mathcal{V}_{c\beta} \psi_\beta]) . \tag{4.31}$$

The variational expression is obtained by replacing $\psi_{\vec{k}}^{(-)}$ by a trial continuum function $\psi_{\vec{k}t}^{(-)}$.

At this stage we have a variational procedure for calculating each of the matrix elements which enter into the evaluation of the transition amplitudes in the model set up in Sec. II B. With regard to the choice of trial functions the procedure would be essentially identical to that used, with considerable success in the past, in the variational approach to atomic bound-state and scattering problems. The point we would emphasize, then, in conclusion, is that a large body of computational experience, developed originally for the calculation of atomic binding energies and scattering parameters, can be taken over to the problem of calculating multiphoton transition probabilities in perturbation theory, and also to provide numerical tests of a nonperturbative model.

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*Supported by the National Science Foundation, Grant No. MPS 75-00131 and by the Office of Naval Research, Contract No. N00014-76-C-0317.

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