Analytical solutions for laser excitation of multilevel systems in the rotating-wave approximation*

T. H. Einwohner, J. Wong, and J. C. Garrison
Lawrence Livermore Laboratory, University of California, Livermore, California 94550
(Received 14 April 1976)

For a multilevel atom or molecule irradiated by a finite superposition of monochromatic fields, the time-dependent rotating-wave-approximation Schrödinger equation can be reduced to an eigenvalue problem when the detunings satisfy a consistency condition. This condition is analyzed and the reduction performed using a graph associated with the interaction Hamiltonian.

I. INTRODUCTION

The rotating-wave approximation[1] has long been used to simplify the description of single-photon excitation of atoms and molecules by weak fields. Even with this simplification, solving for the wave function or density matrix is complicated by the time dependence of the Hamiltonian. In this paper the method used to eliminate the time dependence of the Hamiltonian for particular three- and four-level systems will be generalized. A criterion for the success of the method will be given.

We seek an analytical solution for the wave function $\psi(t)$ of a quantum system with Hamiltonian $H_0+H'(t)$, where H_0 is the Hamiltonian of the unperturbed system with energies $\{E_\alpha\}$ and eigenfunctions $\{\phi_\alpha\}$, $\alpha=1,\ldots,N$. The contribution $H'(t)$ is the dipole interaction $-\vec{d}\cdot\vec{\mathcal{E}}$ between the molecule of dipole moment $\vec{d}$ and a polychromatic electric field representing the light. The field is assumed to be of the form

$$\vec{\mathcal{E}}=\sum_{f=1}^{F}\mathrm{Re}(\vec{\mathcal{E}}_f e^{-i\omega_f t}),$$

where the complex constant $\vec{\mathcal{E}}_f$ measures the amplitude, phase, and polarization of the plane wave with frequency ω_f; i.e., the source linewidth is neglected. A simplifying and not too restrictive assumption is that each of the distinct frequency components of the field is in approximate resonance with at least one allowed molecular transition and that the frequencies are sufficiently separated so that no two frequencies are in approximate resonance with the same transition.

If $\psi(t)$ is expanded as ($\hbar=1$)

$$\psi(t)=\sum_\alpha C_\alpha(t)\phi_\alpha e^{-itE_\alpha},$$

then

$$i\dot{C}_\alpha=\sum_\beta H^{(1)}_{\alpha\beta}(t)C_\beta, \tag{1}$$

where

$$H^{(1)}_{\alpha\beta}\equiv e^{itE_{\alpha\beta}}(\phi_\alpha,H'(t)\phi_\beta)$$
$$=-\frac{1}{2}\sum_f\left((\vec{d}_{\alpha\beta}\cdot\vec{\mathcal{E}}_f)e^{it(E_{\alpha\beta}-\omega_f)}+(\vec{d}_{\alpha\beta}\cdot\vec{\mathcal{E}}_f^{\,*})e^{it(E_{\alpha\beta}+\omega_f)}\right), \tag{2}$$

and $E_{\alpha\beta}\equiv E_\alpha-E_\beta$. Let $\theta_{\alpha\beta}$ be 1 if there is an ω_f close to resonance with $E_{\alpha\beta}$; otherwise, let $\theta_{\alpha\beta}$ be 0. If $\theta_{\alpha\beta}=1$, let the ω_f and $\vec{\mathcal{E}}_f$ of the component of the field in approximate resonance with transition $\alpha\leftrightarrow\beta$ be denoted by $\omega_{\alpha\beta}$ and $\vec{\mathcal{E}}_{\alpha\beta}$,

$$\Delta_{\alpha\beta}\equiv E_{\alpha\beta}-\omega_{\alpha\beta}\eta_{\alpha\beta}\quad(\alpha\neq\beta),$$
$$\Delta_{\alpha\alpha}\equiv 0, \tag{3}$$

where

$$\eta_{\alpha\beta}\equiv E_{\alpha\beta}/|E_{\alpha\beta}|.$$

A frequency ω_f is said to be close to resonance with an allowed transition between levels α and β if $||E_{\alpha\beta}|-\omega_f|\leq\lambda\bar{\omega}$, where $\bar{\omega}$ is a typical frequency and $\lambda=O(\vec{d}_{\alpha\beta}\cdot\vec{\mathcal{E}}_f/\bar{\omega})$. In the rotating-wave approximation the quantity $H^{(1)}_{\alpha\beta}$ is replaced by

$$\bar{H}^{(1)}_{\alpha\beta}(t)\equiv M^{(1)}_{\alpha\beta}e^{it\Delta_{\alpha\beta}}, \tag{4}$$

where

$$M^{(1)}_{\alpha\beta}=-\tfrac{1}{4}\theta_{\alpha\beta}[(1+\eta_{\alpha\beta})(\vec{d}_{\alpha\beta}\cdot\vec{\mathcal{E}}_{\alpha\beta})+(1-\eta_{\alpha\beta})\vec{d}_{\alpha\beta}\cdot\vec{\mathcal{E}}^{\,*}_{\alpha\beta}].$$

It is seen that only those terms of $H^{(1)}_{\alpha\beta}$ are kept for which $\omega_{\alpha\beta}$ is close to resonance with $E_{\alpha\beta}$ and for which the complex variable $e^{\pm i\omega_f t}$ rotates with time in the same direction as $e^{iE_{\alpha\beta}t}$. Equation (4) can be derived[2] from (2) by averaging over a time scale long compared to $\omega^{-1}_{\alpha\beta}$ but short compared to $\Delta^{-1}_{\alpha\beta}$, assuming that these scales are very different. Generalizing this averaging procedure has yielded a multiple-time-scales perturbation theory[3] which extends the rotating-wave approximation.

II. ELIMINATING EXPLICIT TIME DEPENDENCE FROM $\bar{H}^{(1)}$

The substitution in Eq. (1) of (4) and

$$B_\alpha = e^{i\gamma_\alpha t} C_\alpha , \tag{5}$$

where the γ_α are parameters to be determined, yields

$$i\dot{B}_\alpha = \sum_\beta M^{(2)}_{\alpha\beta} e^{it(\gamma_\alpha - \gamma_\beta + \Delta_{\alpha\beta})} B_\beta ,$$

where

$$M^{(2)}_{\alpha\beta} = M^{(1)}_{\alpha\beta} - \gamma_\alpha \delta_{\alpha\beta} . \tag{6}$$

Thus any choice of γ_α such that for all α, β

$$(\gamma_\alpha - \gamma_\beta + \Delta_{\alpha\beta})\theta_{\alpha\beta} = 0 \tag{7}$$

removes the time dependence from $\bar{H}^{(1)}$, yielding the solution

$$B = e^{-itM^{(2)}} C(0) \tag{8}$$

and reducing the solving of (1) to an eigenvalue analysis of the Hermitian matrix $M^{(2)}$. Substitution (5) has been used for two-, three-, and four-level systems.[4] In general (7) involves up to $\frac{1}{2}N(N-1)$ simultaneous equations in the N unknowns γ_α, so that a consistent choice of γ is not always possible. The rest of this paper is concerned with deciding when $\{\gamma_\alpha\}$ can be chosen to satisfy (7) and with actually choosing the $\{\gamma_\alpha\}$.

The dynamics of the interacting system will be pictured by a graph, which is a simplified energy-level (Grotrian) diagram.[5] An (undirected) graph is associated with $\bar{H}^{(1)}$ by associating a vertex of the graph with each energy level and drawing an edge between vertices α and β when $M^{(1)}_{\alpha\beta} \neq 0$. A simple example (Fig. 1) has vertices $1, \ldots, 8$, and a representative edge, say 34, means that level 4 is directly accessible from level 3 in the rotating-wave approximation. The graph has "pendant" (one-edge) vertices 2, 8, 5 and a "cycle" (14371).[6]

For acyclic graphs ("trees") the number of edges turns out to be one less than the number of vertices, so that the set $\{\gamma_\alpha\}$ can be chosen to satisfy (7). An explicit construction (shown by the arrows in Fig. 1 with edge 17 temporarily ignored to avoid cycles) is as follows: (i) For each pendant vertex, such as 8, direct the incident edge, 86, toward the adjacent vertex, 6, and call that vertex the "successor" of the pendant vertex considered. (ii) Delete all pendant vertices and directed edges. (iii) Repeat steps (i) and (ii) until the tree has been "pruned" to a single "end" vertex (3 in Fig. 1). In this process each vertex save the end vertex τ has a unique successor. (iv) Assign to τ an arbitrary real γ_τ and to each other vertex α a $\gamma_\alpha = \gamma_\beta - \Delta_{\alpha\beta}$, where β is the successor of α. Thus any $\bar{H}^{(1)}$ with an acyclic graph can be solved exactly.

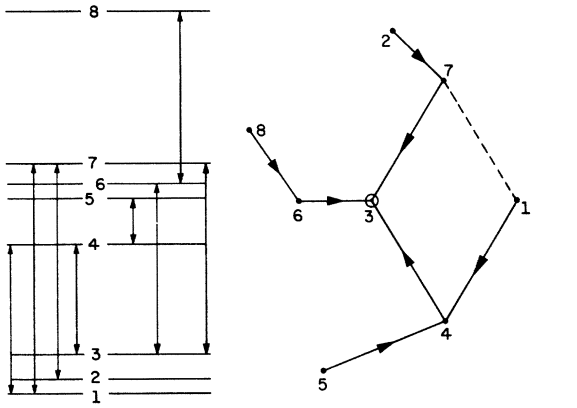

FIG. 1. Energy-level diagram (left-hand side) and its graph (right-hand side). Levels 1–8 represent the 6^3P_0, 6^3P_1, 6^3P_2, 7^3S_1, 7^3P_2, 6^3D_3, 8^3S_1, and 5^3F_3 levels of Hg I, respectively (Ref. 5). Double-headed arrows represent transitions close to resonance with frequencies of the polychromatic light. Dotted line 17 is an edge of the graph but is ignored in the tree-graph "pruning" operation described in the text.

For cyclic graphs the pruning operation leads not to end vertices but to cycles, or possibly cycles joined by a single bridge (a shape reminiscent of eyeglass frames). Even for cyclic graphs the pruning operation (or a simple extension for bridged cycles) has shown that a consistent assignment of $\{\gamma_\alpha\}$ on cycles assures a consistent assignment of $\{\gamma_\alpha\}$ for the whole graph. The assignment of $\{\gamma\}$ to the vertices $\{\alpha_\tau\}$ in a cycle $(\alpha_1\alpha_2\cdots\alpha_L\alpha_1)$ is consistent if

$$\Delta \equiv \sum_{\tau=1}^{L} \Delta(\alpha_\tau, \alpha_{\tau+1}) = 0 \quad (\alpha_{L+1} \equiv \alpha_1); \tag{9}$$

that is, given a pair of vertices joined by more than one path, the sum of the detunings along a joining path is independent of the path chosen. If (9) holds for all cycles in the graph, the graph is called "zero-cyclic."

A consistent assignment of γ to cycles in zero-cyclic graphs is $\gamma(\alpha_\tau) = \gamma(\alpha_{\tau+1}) - \Delta(\alpha_\tau, \alpha_{\tau+1})$. Thus a sufficient condition for analytic solution of the rotating-wave approximation is that the graph of $\bar{H}^{(1)}$ be acyclic or zero-cyclic.

III. CONDITIONS FOR ZERO-CYCLIC GRAPHS

For monochromatic light, graphs all of whose cycles are short enough will be proven zero-cyclic. Let $1, \ldots, L$ be the vertices of a cycle. From (3),

$$\Delta \equiv \sum_{\tau=1}^{L} \Delta_{\tau,\tau+1} = \omega_f \sum_{\tau=1}^{L} \eta_{\tau,\tau+1} \quad (\bar{\omega} = \omega_f),$$

since the cycle sum of $E_{\tau,\tau+1}$ is zero. Then $|\Delta|$

$<L\lambda\bar{\omega}$, since each of the L edges represents a transition close to resonance, so that $\sum\eta_{r,r+1}$ is an integer with absolute value less than $L\lambda$. Thus $L\lambda<1$ forces the graph to be zero-cyclic. To show that $L\lambda<1$ is also a necessary condition for all graphs with a given maximum cycle length to be zero-cyclic, construct an example with the energy-level assignment $E_r=r\bar{\omega}$, $0\le r\le m$, and $E_r=m\bar{\omega}(2m-1-r)/(m-1)$, $m<r\le 2m-1$. This assignment leads to a non-zero-cyclic graph if $m=O(1/\lambda)$.

Monochromatic light can give rise to connected graphs (with more than one edge) if the atom or molecule has an equal spacing between consecutive energy levels, such as for a harmonic oscillator. An example leading to cyclic graphs is when each of a group of nearly degenerate levels is approximately in resonance with a pair of levels, i.e., $E_0=0$, $E_1=2\bar{\omega}$, $E_i=(1+k_i\lambda)\bar{\omega}$ for $i=2,\ldots,N$, where $|k_i|<1$. A second source of cyclic graphs in the presence of monochromatic light is a many-electron atom (which has a high density of electronic energy levels) or a polyatomic molecule (which has a high density of vibrational levels due to the large number of vibrational modes). For such systems one is likely to find subsystems of energy levels with approximately equal spacing. These three situations are the only ones which, to our knowledge, lead to connected graphs with monochromatic light.

For polychromatic light, results this simple cannot be obtained. The cycle detuning sum becomes

$$\Delta=\sum_{f=1}^{F}N_f\omega_f,$$

where the integer

$$N_f\equiv\sum_r\eta_{r,r+1}\,\delta(\omega_f,\omega_{r,r+1}),$$

and where δ is Kronecker's delta. The presence of more than one N_f vitiates the above method of proof.

The following example shows that $L\lambda<1$ does not imply a zero-cyclic graph for polychromatic light. Let there be two frequencies, ω_1 and ω_2, with $\delta\omega\equiv\omega_1-\omega_2$ and $|\delta\omega|<\bar{\omega}$. Fix the interaction parameter $\lambda\cong\delta\omega/6\bar{\omega}$ and consider a system of six levels with energies $E_0=0$, $E_1=\omega_1+\frac{1}{6}\delta\omega$, $E_2=\omega_1+\omega_2+\frac{1}{3}\delta\omega$, $E_3=\omega_2+\frac{1}{2}\delta\omega$, $E_4=2\omega_2+\frac{2}{3}\delta\omega$, $E_5=\omega_2-\frac{1}{6}\delta\omega$. For the chosen value of λ the corresponding graph is a hexagon and $L\lambda\approx\delta\omega/\bar{\omega}<1$. However, the cycle detuning sum is found to be $\Delta=\delta\omega\neq 0$; i.e., the graph is not zero-cyclic.

IV. ANALYSIS OF LARGE GRAPHS

For graphs too large or complicated to be analyzed by inspection, the following algorithm will decide if G is zero-cyclic and assign consistent $\{\gamma_\alpha\}$ if it is. Otherwise the algorithm yields a maximal zero-cyclic subgraph G' containing all the vertices of G. The algorithm is a slight generalization of the so-called greedy algorithm for constructing maximal spanning trees.[7]

Assign a real number (weight) to each edge. For zero-cyclic graphs any choice of weights will do. For other graphs the weight $W_{\alpha\beta}$ should reflect the importance of the corresponding term in the differential equations; in particular, it should be an increasing function of $|M^{(1)}_{\alpha\beta}|$, vanishing with $M^{(1)}_{\alpha\beta}$, and a nonincreasing function of $|\Delta_{\alpha\beta}|$. A very simple choice is $W_{\alpha\beta}=|M^{(1)}_{\alpha\beta}|^2$; an alternative is $W_{\alpha\beta}=(1+|\Delta_{\alpha\beta}/M^{(1)}_{\alpha\beta}|^2)^{-1}$, the maximum excited-state population for the two-level system α,β undergoing Rabi oscillations. List the edges of G in order of decreasing weight; then the graph $G'(W)$ is built up from edges selected in turn from the list as follows:

(1) If neither vertex α or β terminating the selected edge $e_{\alpha\beta}$ is in the current G', then $e_{\alpha\beta}$, α and β are added to G'. One vertex α is given arbitrary γ_α, the other a $\gamma_\beta=\gamma_\alpha-\Delta_{\beta\alpha}$.

(2) If $\alpha\in G'$, $\beta\notin G'$, then β and $e_{\alpha\beta}$ are added to G' and $\gamma_\beta=\gamma_\alpha-\Delta_{\beta\alpha}$.

(3) If $\alpha,\beta\in G'$, two possibilities arise: (a) Adding $e_{\alpha\beta}$ to G' would join two previously disconnected components of G'. Then $e_{\alpha\beta}$ is added to G' but the vertices of one component are reassigned to ensure $\gamma_\beta=\gamma_\alpha-\Delta_{\beta\alpha}$. This can always be done, since each component has one arbitrary γ. (b) Vertices α and β are in the same component of G'. Then α and β have previously assigned γ. The edge $e_{\alpha\beta}$ is added to G' if and only if $\Delta_{\alpha\beta}=\gamma_\beta-\gamma_\alpha$.

When the list is exhausted, G' is complete. If no edge has failed test (3b), G is zero-cyclic. If G is not zero-cyclic, G' is by construction a maximal zero-cyclic proper subgraph of G. Note that G' is maximal under graph inclusion; i.e., adding an edge to G' yields a non-zero-cyclic graph.

It is reasonable to ask: Why go to the trouble of completing the construction of G' after the first failure of test (3b)? The interest of G' is that the analytical solution for the wave function corresponding to G' is a candidate for an approximation to the true wave function. In evaluating such candidates one has in mind some measure of error, J, such as some norm of the difference between the respective wave functions, or, for certain applications, the error in the population of a desired energy level. In principle, but at huge

expense for large graphs, one could construct $\mathcal{G}$, the class of all subgraphs of G which are zero-cyclic and maximal under graph inclusion, find by exhaustive search which subgraph minimizes J, and see if the minimum J is acceptable. To avoid the expense of constructing and testing such a large class of subgraphs, the method of weighted edges was used. This yields one maximal subgraph for each choice of the weighting function W. It is not known in advance which choice of W minimizes J or what the minimum J is. For a simple choice of J, however, we can find an upper bound for J and a weight function which minimizes the bound. For each maximal zero-cyclic proper subgraph $\hat{G}$, there is a set $\{\hat{\gamma}\}$ which satisfies (7) for all pairs α,β such that $e_{\alpha\beta}\in\hat{G}$. Then substitution (5) yields

$$i\dot{B}_\alpha = \sum_\beta [M^{(2)}_{\alpha\beta} + M^{(3)}_{\alpha\beta}(t)]B_\beta, \tag{10}$$

where $M^{(2)}_{\alpha\beta}$ is given by (6) if $e_{\alpha\beta}\in\hat{G}$ and vanishes otherwise. The element $M^{(3)}_{\alpha\beta}$ is $M^{(1)}_{\alpha\beta}e^{it(\gamma_\alpha-\gamma_\beta+\Delta_{\alpha\beta})}$ if $e_{\alpha\beta}\notin\hat{G}$ and vanishes otherwise.

Let the error measure be

$$J = \sum_\alpha |i\dot{B}_\alpha - \{[M^{(2)}+M^{(3)}(t)]B\}_\alpha|^2. \tag{11}$$

Its value for trial wave function $B(\hat{G}) = e^{-itM^{(2)}(\hat{G})}C(0)$ is

$$J(\hat{G}) = \sum_\alpha |M^{(3)}(\hat{G})e^{-itM^{(2)}(\hat{G}}C(0)|^2 \le \max_{\alpha\beta} |M^{(3)}(\hat{G})_{\alpha\beta}|^2,$$

and $J' = \min J(\hat{G})$ (over $\hat{G}$) satisfies

$$J' \le \min\max_{\alpha\beta} |M^{(3)}(\hat{G})_{\alpha\beta}|^2 = \min\max_{\alpha\beta}(|M^{(1)}_{\alpha\beta}|^2 : e_{\alpha\beta}\in\hat{G}).$$

The latter quantity is minimized by the "greedy" algorithm for the weighting function $W_{\alpha\beta} = |M^{(1)}_{\alpha\beta}|^2$. The maximal zero-cyclic proper subgraph thus generated by the "greedy" algorithm will yield a wave function which is a good or bad approximation depending on whether the heaviest rejected edge is heavy or light compared to a typical accepted edge. If, for example, the graph is a square with all edges of approximately equal values of $|M^{(1)}_{\alpha\beta}|$, the maximal zero-cyclic proper subgraph will yield a poor wave function. On the other hand, if the graph would be zero-cyclic but for one edge of vanishingly small $|M^{(1)}_{\alpha\beta}|$, the maximal zero-cyclic proper subgraph would yield a good approximate wave function. The error estimate above is crude, because the quantity minimized is an upper bound for J, not J itself.

Another possible use of wave functions derived from maximal zero-cyclic proper subgraphs is that one can form linear combinations of such wave functions which are better approximations. For the above example of the non-zero-cyclic square, one would take linear combinations of the wave functions obtained from the four graphs obtained by removing an edge from the square. In general one would, in principle, take linear combinations

$$C(\mu) = \sum_{G''\in\mathcal{G}} \mu(G'';t)C(G'';t)$$

and find the minimum over μ of

$$J^{(1)}(t) \equiv \sum_\alpha \left(\left| i\dot{C}_\alpha - \sum_\beta H^{(1)}_{\alpha\beta}C_\beta \right|^2 + \Lambda(t)|C_\alpha|^2 \right),$$

where $C(G'';t)$ is the analytical wave function from the maximal zero-cyclic subgraph G'' and Λ is a Lagrange multiplier associated with the normalization of C. One way to find the μ corresponding to the minimum $J^{(1)}$ for $0<t<T$ is to choose a set of interpolation points t_i and minimize $J^{(1)}(t_i)$, obtaining $\mu(G'',t_i)$. For other t, the appropriate μ and desired averages of the wave function could then be determined by interpolation. In practice it would be more economical to guess at a small set of maximal zero-cyclic proper subgraphs.

V. EXTENSION TO THE DENSITY MATRIX

For systems not initially in a pure state, it is more convenient to work with the density matrix

$$\rho_{\alpha\beta}(t) = \langle C_\alpha C^*_\beta\rangle_0,$$

where the average is over an appropriate ensemble at $t=0$. The above-described methods can also solve equations for $\rho_{\alpha\beta}$, even if a simple phenomenological decay term is included. The appropriate equation[8]

$$i\dot{\rho}_{\alpha\beta} = [M^{(1)},\rho]_{\alpha\beta} - i\Gamma_{\alpha\beta}\rho_{\alpha\beta}$$

can, for zero-cyclic graphs, be reduced by the substitution

$$B_{\alpha\beta} = e^{it(\gamma_\alpha-\gamma_\beta)}\rho_{\alpha\beta}$$

to

$$i\dot{B}_{\alpha\beta} = \sum_\gamma (M^{(2)}_{\alpha\gamma}B_{\gamma\beta} - M^{(2)}_{\gamma\beta}B_{\alpha\gamma}) - i\Gamma_{\alpha\beta}B_{\alpha\beta}. \tag{12}$$

If $\Gamma_{\alpha\beta} = \Gamma_\alpha + \Gamma_\beta$, corresponding to inclusion of a $-i\Gamma_\alpha C_\alpha$ in the right-hand side of (1), the solution of (10) is

$$B(t) = e^{-it(M^{(2)}-i\Gamma)}\rho(0)e^{it(M^{(2)}+i\Gamma)},$$

where Γ is a diagonal matrix with elements Γ_α. If $\Gamma_{\alpha\beta}$ is more general, B must be considered an $N^2\times 1$ vector, $\Gamma_{\alpha\beta}$ elements of a diagonal $N^2\times N^2$

matrix, and $M^{(2)}_{\alpha\gamma}$ and $M^{(2)}_{\gamma\beta}$ elements of a sparse $N^2 \times N^2$ matrix. Solution of (10), although possible in principle, is for large N more difficult in practice.

VI. POSSIBLE APPLICATIONS

The systematic analysis of large graphs is particularly suited to the study of low-intensity photoexcitation of atoms and molecules with complex spectra, such as heavy atoms or molecules with more than two or three atoms. An example is the isotope-selective photodissociation of SF_6 by an infrared laser.[9] The large ratio of dissociation to photon energy suggests a multistage process, while the low intensity used suggests the validity of the rotating-wave approximation. Were energy levels and matrix elements known, the above-described methods could be used to study the photoexcitation part of that process. Standard graph-theoretical techniques can determine which energy levels are accessible from the ground state. In a complex graph with many branches and cycles some fraction of the incident light energy will be used to populate levels other than the target level. The methods developed here can be used to attack the problem of minimizing this waste of energy.

ACKNOWLEDGMENTS

We learned about the "greedy " algorithm for constructing maximal spanning trees in an introductory course on graph theory given by Kellogg S. Booth. We thank him for pointing out Ref. 7. We also thank R. J. Harrach for suggestions on improving the clarity of the manuscript.

---

*Work performed under the auspices of the U. S. Energy Research and Development Administration under Contract No. W-7405-Eng-48.

[1]F. Bloch and A. Siegert, Phys. Rev. 57, 522 (1940); A. Maitland and M. H. Dunn, *Laser Physics* (North-Holland, Amsterdam, 1969), p. 78.

[2]S. Flugge, *Practical Quantum Mechanics* (Springer, New York, 1971), Vol. II, p. 138.

[3]J. Wong, J. C. Garrison, and T. H. Einwohner, Phys. Rev. A 13, 674 (1976).

[4]W. R. Bennett, Jr., Phys. Rev. 126, 580 (1962); I. M. Beterov and V. P. Chebotaev, in *Progress in Quantum Electronics*, edited by J. H. Sanders and S. Stenholm (Pergamon, New York, 1975), Vol. 3, p. 16; J. Shirley, J. Appl. Phys. 34, 783 (1963); R. J. Harrach, Natl. Bur. Stand. Tech. Note No. 346 (1966).

[5]W. Grotrian, *Graphische Darstellung der Spektren von Atomen und Ionen mit Ein, Zwei und Drei Valenzelektronen* (Springer, Berlin, 1928), as described by G. Herzberg [*Atomic Spectra and Atomic Structure* (Dover, New York, 1944), p. 202].

[6]This terminology is widely used in graph theory. Discussion has been restricted to connected graphs. A disconnected graph corresponds to uncoupled subsystems of differential equations. Thus each connected component of a graph can be treated separately.

[7]J. B. Kruskal, Jr., Proc. Am. Math. Soc. 7, 48 (1956).

[8]M. Sargeant III, M. O. Scully, and W. E. Lamb, Jr., *Laser Physics* (Addison-Wesley, Reading, Mass., 1974), p. 85.

[9]R. V. Ambartzumian, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Zh. Eksp. Teor. Fiz. Pis'ma Red. 21, 375 (1975) [JETP Lett. 21, 171 (1975)].