Multiphoton Processes in Intense Laser Fields*

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An introduction to several recent new developments in semiclassical Floquet theories and quasi-energy methods for perturbative and nonperturbative treatments of intense field multiphoton excitation (MPE), ionization (MPI), and dissociation (MPD) of atoms and molecules is presented.

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I. INTRODUCTION

There is currently much interest in what is commonly referred to as intense-field problems. Among these problems, two areas are of special interest to atomic and molecular physics. The first is concerned with the structure and dynamics of Rydberg atoms in strong external dc electric and/or magnetic fields. Subjects such as diamagnetism in highly excited states, dynamical symmetry in Zeeman problem, quasi-Landau resonances, autoionization resonances in electric and/or magnetic fields, etc., are topics of current intensive studies.¹ For the most part, these problems involve external magnetic and/or electric fields combined with a Coulomb field such that all fields make comparable contributions to the basic forces and energies. Thus we are dealing with situations for which conventional perturbation theory is no longer adequate. The other area of intense field problems of current importance is concerned with the study of multiphoton interactions of lasers with atoms and molecules. The development of intense and powerful tunable lasers has revolutionized optical spectroscopy and led to the discovery of many distinctly new nonlinear molecular phenomena, foremost among which is collisionless multiphoton ionization (MPI) of atoms and molecules and multiphoton excitation (MPE) and dissociation (MPD) of polyatomic molecules.
Although the qualitative features of the MPI/MPE/MPD processes appear to be established, quantitative analysis of the underlying quantum dynamics remains a major challenge. The main obstacles stem from the complexity of the molecular level structure and the lack of suitable theoretical and numerical methods.

The theory of multiphoton processes can be formulated in a fully quantum mechanical or semiclassical formalism. In the former approach, both the system and the field are treated quantum mechanically, while in the semiclassical approach, the system is described by a time-dependent Schrödinger equation in which the effect of the radiation field is represented by an effective Hamiltonian consistent with Maxwell's equations. The semiclassical approach usually leads to Hamiltonians periodic in time through an assumed sinusoidal time variation of the electromagnetic field. In addition to being considerably more tractable, the semiclassical theory has been shown to lead to results that are equivalent to those obtained from the fully quantized theory in strong fields. Indeed much recent multiphoton research is couched in terms of semiclassical theory, particularly the Floquet theoretical approach. In this article, a short account of several new developments in Floquet theory and quasi-energy methods recently carried out at the University of Kansas will be described. For more detailed discussions, we refer the reader to the original articles referenced and to the more extensive review article which includes also discussions of other Floquet developments.

II. MULTIPHOTON EXCITATION OF FINITE-LEVEL SYSTEMS

The solutions of the differential equations of a quantized system interacting with a sinusoidal monochromatic field can be written as a Fourier series. As long ago as 1883–1900, Floquet was studying the solutions of such linear differential equations with periodic coefficients and Poincaré was considering the construction of the solutions. The Floquet theorem was later used by Autler and Townes to obtain the wave function for the two-level system in terms of infinite continued fractions. However, application of Floquet theory to quantum systems began to grow only after the mid 1960's. In a well-known paper, Shirley reformulated the problem of the interaction of a two-level quantum system with a strong oscillating field by relating the solution of the Schrödinger equation to a time-independent infinite Floquet matrix. While this is literally a semiclassical theory that does not involve explicit field quantization, Shirley shows that his Floquet states can be interpreted physically as quantum field states. Indeed his Floquet quasienergy diagram is identical to the dressed-atom picture derived by Cohen-Tannoudji and Haroche.

Exact analytical solution of the time-dependent Schrodinger equation with temporally periodic Hamiltonian is possible only in exceptional cases. Thus it is in general necessary to develop approximate methods for the treatment of multiphoton excitation (MPE) of atoms and molecules.

Shirley's Floquet matrix method, which is equivalent to summing the entire perturbation expansion to all orders, can be extended to the non-perturbative study of rovi-
brational multiphoton excitation of a molecule within a single electronic state. In the electric dipole approximation, the interaction potential energy between the quantum system and the classical field is given by

$$V(\vec{r},t) = -\mu(\vec{r}) \cdot \vec{E}_0 \cos(\omega t + \delta),$$

where $\mu$ is the dipole moment operator of the molecule, $E_0$ and $\delta$ are the field amplitude and phase, respectively, assumed to be independent of time, and $\vec{r}$ represents the internuclear coordinates. The Floquet matrix possesses a block tridiagonal form as shown in Fig. 1.

$$[H_F] = \begin{pmatrix}
A + 2\omega l & B & 0 & 0 & 0 & n = -2 \\
B & A + \omega l & B & 0 & 0 & n = -1 \\
0 & B & A & B & 0 & n = 0 \\
0 & 0 & B & A - \omega l & B & n = -1 \\
0 & 0 & 0 & B & A - 2\omega l & n = -2
\end{pmatrix}$$

Where

$$A = \begin{pmatrix}
E_{00}^{(0)} & 0 & 0 & 0 & 0 & n = 0 \\
0 & E_{10}^{(0)} & 0 & 0 & 0 & n = -1 \\
0 & 0 & E_{20}^{(0)} & 0 & 0 & n = -2
\end{pmatrix}$$

$$B = \begin{pmatrix}
0 & b_{00,01} & 0 & 0 & 0 & n = 0 \\
0 & b_{00,01} & 0 & 0 & 0 & n = -1 \\
0 & 0 & b_{00,01} & 0 & 0 & n = -2
\end{pmatrix}$$

FIG. 1 Structure of the Floquet Hamiltonian for multiphoton excitation of diatomic molecules. The Hamiltonian is composed of the diagonal Floquet blocks, of type A, and off-diagonal blocks of type B. $E_{ij}^{(0)}$ are the unperturbed vibration-rotational energies, and $b_{ij,j'} = -1/2 < v_j | \mu \cdot \vec{E}_0 | v_{j'} > e^{i\delta}$, with $\mu$ the electric dipole moment operator, and $E_0$ the peak amplitude and $\delta$ the phase of the monochromatic field.

The determination of the vibrational-rotational quasi-energies and quasi-energy states (QES) thus reduces to the solution of a time-independent Floquet matrix eigenproblem. Fig. 1 shows that $H_F$ has a periodic structure with only the number of $\omega$'s in the diagonal elements varying from block to block. This structure endows the quasi-energy eigenvalues and eigenvectors of $H_F$ with periodic properties.
Much information can be gained from the plot of the quasi-energy eigenvalues (or the characteristic exponents) of the Floquet Hamiltonian. The main feature of the quasi-energy plot is illustrated in Fig. 2 for the simple case of a two-state system of energy spacing $\hbar \omega_0$ subjected to the dipole interaction $V(t) = 2b \cos \omega t$ with an intense monochromatic field of frequency $\omega$. In Fig. 2a, six of the quasi-energies $\epsilon$ are plotted as a function of the level-spacing $\omega_0$, using $\omega$ as a scaling parameter. The corresponding time average transition probability $\overline{P}$ is shown in Fig. 2b. One notices that resonance occurs (near $\omega_0 = \omega$, $3\omega$, $5\omega$, $7\omega$) whenever the quasienergy curves for two eigenvalues approach each other closely but do not cross (avoided or anti-crossing). The minimum separation of two branches of the (quasi-energy) hyperbola is correlated with the width of the resonance peak, whereas the location of the minimum separation determines the resonance position. At this rather high field strength, $b = \omega/3$, all four resonances are clearly seen to be substantially shifted from their respective unperturbed positions (the Bloch-Siegert shifts$^{15}$). The one-photon peak is further strongly broadened, although the five- and seven-photon peaks remain discrete and are much narrower in width. As one increases the coupling strength $b$, each resonance in Fig. 2b further broadens and shifts toward smaller values of $\omega_0$ (Fig. 3) until it becomes lost in the ever-widening background.

Chu et al.$^{16}$ have recently extended the Floquet matrix method to include the effect of an additional external static electric field. The quasi-energy and MPE spectra of the HF molecule are studied as functions of field strengths and frequency. Nonlinear effects such as power broadening, dynamical Stark effect, Autler-Townes multiplet splitting, hole burning, and S-hamp behaviors, etc., are observed and discussed in terms of quasi-energy diagrams.
FIG. 3 Time-averaged transition probabilities $\bar{P}_{\alpha \rightarrow \beta}$ as a function of $\omega_0$ with (a) $b/\omega = 1/3$, (b) $b/\omega = 2/3$, and (c) $b/\omega = 1.0$. Note the power-broadening and ac-Stark-shift effects as $b$ increases. Notations same as Fig. 2.

(Fig. 4). Many of the salient features in the spectral line shapes may be qualitatively understood in terms of an analytical three- or four-level model.\textsuperscript{17} The addition of a dc electric field removes the restriction of the rotational dipole selection rule and causes significant intermixing of the bare molecular vibrator states. Due to the greater number of strongly coupled nearby states in the dc field, non-linear optical effects such as those mentioned above appear at a much lower ac field strength than they would in the absence of the dc field. The introduction of an external dc field, therefore, strongly enhances the MPE probabilities and results in a much richer spectrum, in accord with the experimental observation.\textsuperscript{18}

Shirley's Floquet Hamiltonian method, powerful as it may be, is subject to some practical limitations. In dealing with molecular multiphoton problems, the Floquet matrix is truncated to N by N dimensions where $N = N_F N_v N_J$, where $N_F$ is the number of Floquet photon blocks, $N_v$ is the number of rotational states included in one vibrational level (Fig. 1). As N increases rapidly with the size of the molecule and with the order of multiphoton processes, and as the computational expense grows as $N^3$, the full Floquet analysis can become prohibitively costly even for simple diatomic molecules. One is thus led to seek new approximate techniques capable of providing accurate results yet involving much smaller Floquet matrix manipulations. The situation here is analogous to the field of molecular collision theory: where a variety of angular momentum decoupling methods (for recent
reviews, see Refs. 19) have been developed in the past decade to alleviate the problem of a large number of coupled equations. In the following subsections, some of the recently developed approximate Floquet treatments will be described.

![Graph](image)

**FIG. 4** Quasienergy plots (a) and time-average MPE transition probabilities $\overline{P}_{00 \rightarrow v_j}$ (b) for the HF molecule subjected to both the laser ($E_{ac} = 1.0$ TW/cm$^2$) and the dc electric fields ($E_{dc} = 10^{-4}$ au) simultaneously. Dot-dash lines indicate one-photon peaks, dashed lines are two-photon peaks, and solid lines are three-photon peaks. Nonlinear effects such as power broadening, dynamical Stark shift, Autler-Townes multiplet splitting, hole burning, and S-hump behaviors, etc., are observed and can be correlated with the quasienergy diagram. The introduction of an external dc field strongly enhances the MPE probabilities and results in a much richer spectrum.

A. **Nonadiabatic theory for resonant multiphoton excitation**

Recently, we have initiated the development of an efficient yet reliable method for nonperturbative treatment of nonlinear multiphoton absorption (MPA) in intense infrared (IR) laser fields.20 The approach is based on the adiabatic separation of fast vibrational motion from slow rotational motion, incorporating the fact that the IR laser frequency is close to the frequencies of adjacent vibrational transitions. One thus first solves the quasi-vibrational energy (QVE) states (or, equivalently, the dressed vibrational states) with molecular orientation fixed. This reduces the computationally often formidable (vibrational-rotational) Floquet matrix analysis to a manageable scale, and, in addition, provides useful physical insights for understanding the nonlinear MPA dynamics. The QVE levels are found to be grouped into distinct energy bands, characterized by the IR frequency, with each band providing an effective potential for molecular rotation. Whereas the interband
couplings are totally negligible, the intraband nonadiabatic angular couplings are the main driving mechanisms for inducing resonant vibrational-rotational multiphoton transitions. The utility of the method is illustrated by a detailed study of the sequential MPA spectra for $^{12}$C$^6$O molecule, including state-to-state multi-quantum transitions and transitions from initially thermally distributed states as a whole (Fig. 5). Excellent agreement between the MPA spectra obtained by the nonadiabatic approach and by the exact Floquet matrix method was observed in every detail. Since the nonadiabatic approach is usually computationally order(s) of magnitude faster than the exact Floquet analysis, it may provide a practical nonperturbative method for generating high resolution resonant MPA spectra of small polyatomic molecules.

![Graphs showing MPE transition probabilities](image)

**FIG. 5** Time-averaged MPE transition probabilities for the CO molecules initially prepared at states $| v = 0, j = 3, m_j >$ with (a) $m_j = 0$, (b) $m_j = 1$, (c) $m_j = 2$, and (d) $m_j = 3$, respectively, at 50 GW/cm$^2$ of laser field strength. Note the change of the spectra as the rotational magnetic quantum number $m_j$ (which is a constant of motion) varies. Line patterns same as Fig. 4.

B. Most probable path approach

The most probable path approach was introduced recently by Tietz and Chu in an ab initio study of high-order multiphoton excitation of the SO$_2$ molecule. The feasibility of multiphoton excitation (MPE) and dissociation (MPD) of triatomic molecules is a controversial subject among experimentalists. Some groups have reported experimental observations of collisionless MPD in triatomic molecules (SO$_2$, O$_3$, OCS) at 1 GW/cm$^2$ laser field strength range, while others have disputed these claims. It is therefore desirable to
carry out comprehensive theoretical studies of the MPE/MPD dynamics of these sparse to intermediate case molecules.

A brute-force attempt to calculate polyatomic MPE would quickly become impossible due to the large size of the Floquet matrix needed for convergence. For typical ten-photon calculations for $\text{SO}_2$, for example, a matrix on the order of $5000 \times 5000$ would have to be diagonalized at each frequency and field strength. In any exact Floquet calculation, however, the majority of the molecule-field states are unimportant due to extreme detuning or very small coupling matrix elements. The most probable path approach (MPPA) is a practical strategy introduced to determine which molecule-field states are, in fact, important at each step of the multiphoton processes. The procedure is derived from algorithms which utilize artificial intelligence to prune the number of choices at each node (photon order) of a decision tree. Similar to some minimax game playing programs, the MPPA examines the possible paths to take at each photon order iteration with the static evaluation function given by $N$th-order perturbation theory (this is a breadth-first search). If all paths were followed exhaustively, the problem would be beyond practical solution. In game theory, one solution is to ignore those paths that start with very poor moves. The MPPA likewise uses a breadth-limiting heuristic technique and discards any paths for which the $N$th order coupling term is small (with respect to other $N$th-order terms).

The MPPA begins by calculating all possible second-order perturbative terms. The $N_p$ largest couplings (where $N_p$ is the number of paths to keep at each step) are chosen as the most probable paths through second order. The initial state (of course) and the intermediate states of the chosen paths are marked as important and are used in the final calculations. At each iterative step, the method calculates all possible $(N + 1)$ st-order couplings (paths) using only the $N_p$ Nth-order paths saved in the last iteration. The $(N + 1)$ st-order couplings are then examined and the largest $N_p$ are saved for further traversal. Nth-order states which have now become intermediate to a large $(N + 1)$ st-order path are "important" and are marked for later use. By iterating long enough, one can traverse the entire Floquet molecule-field basis space, saving only those states that are important to the various $i$th-order processes. The reduction of the basis set is quite substantial and leads to many orders of magnitude savings in computer time, while still maintaining good accuracy in most cases.

Using the MPPA, Tietz and Chu found that collisionless MPD of $\text{SO}_2$ is not achievable at laser intensities under 20 GW/cm$^2$ (Fig. 6), in agreement with the recent experimental results of Simpson and Bloembergen. The latter experiment, however, extended the laser power up to 300 GW/cm$^2$, and found that appreciable MPD yields begin to occur, and that the process is controlled by the laser intensity and not the laser fluence. Further MPPA study showed that MPE of $\text{SO}_2$ is primarily a one-ladder pumping phenomenon dominated by the power broadening effect and that MPD is likely to occur (though the yield is predicted to be small, $P < 10^{-3}$) at laser intensities above 100 GW/cm$^2$.

Several other quantum-mechanical MPE studies of triatomic molecules have appeared recently. Quack and Sudiloff have studied the possibility of mode-selective IR-MPE of $\text{O}_3$, using a quasi-resonant approximation, in which they neglect interactions with states that are off-resonance by more than $\omega/2$. Milfeld and Wyatt have studied the MPE of
OCS, using the Magnus approximation in the Floquet Hamiltonian.

![Graph showing the dependence of the average number of photons absorbed by SO₂ on excitation laser intensity.](image)

**FIG. 6** Dependence of the average number of photons absorbed (\(\bar{n}\)) by SO₂ on excitation laser intensity. The different traces correspond to the indicated excitation frequencies (cm\(^{-1}\)) of the laser. Typical IR MPD of SO₂ requires about forty 9.3 \(\mu\)m photons. The results shown in this figure indicate that MPD of SO₂ cannot be achieved for \(I < 20\) GW/cm\(^2\).

It appears that detailed ab initio studies of the MPE dynamics in small polyatomic molecules are now becoming feasible. Such theoretical investigations would provide useful new physical insights and complementary information to the experimental results.

### III. NON-HERMITIAN FLOQUET THEORY

The Floquet matrix methods described in Sec. II involving time-independent Hermitian Floquet Hamiltonian provide nonperturbative ab initio techniques for the treatment of bound-bound multiphoton transitions. These methods cannot, however, be applied to bound-free transitions such as multiphoton excitation (MPI) or dissociation (MPD) processes. A major recent extension of the Floquet theory is to generalize the conventional (finite-level) dressed-atom or quasi-energy picture to include the complete set of bound and continuum states of atoms and molecules. This has the effect of giving each of the dressed or quasienergy levels an intensity-dependent imaginary part (width) in addition to the usual field-induced shift. Proper interpretation of the frequency and intensity dependence of the complex quasi-energies give rise to MPI or MPD rates.

A complex quasi-vibrational energy formalism\(^{29,30}\) has been recently developed for
the nonperturbative treatment of intense field molecular multiphoton dissociation. This involves the use of two major conceptualizations — complex coordinate transformation\(^3\)\(^1\),\(^3\)\(^2\) and \(L^2\)-continuum discretization\(^3\)\(^3\) — which have been discussed previously in our study of multiphoton ionization (MPI) of atoms.\(^3\)\(^4\),\(^3\)\(^5\) The complex eigenvalue parameters are of the appropriately analytically continued, time-independent non-Hermitian molecular Floquet Hamiltonian\(^2\)\(^9\),\(^3\)\(^0\) as obtained via the complex-coordinate transformation \(R \rightarrow R \exp (i \theta)\), Fig. 7. Such a transformation distorts the continuous spectrum away from the real axis, exposing the Stark resonances (or, equivalently, the dressed molecular states or complex quasi-vibrational energy (QVE) states) in appropriate higher Riemann sheets, and also allows use of finite variational expansions employing \(L^2\) basis functions chosen from a complete discrete basis. The use of a complete discrete \(L^2\) basis obviates the necessity to explicitly introduce exact molecular bound and continuum states, thus reducing all computations to those involving finite-dimensional non-Hermitian matrices. The real part of the complex QVE provides ac-Stark shifted vibronic energy, whereas the imaginary part determines the photodissociation or MPD rate.

\[
\begin{array}{c|c|c|c|c}
 A & 4\omega I & B & 0 & 0 \\
 B^T & A - 2\omega I & B & 0 & 0 \\
 0 & B^T & A & B & 0 \\
 0 & 0 & B^T & A - 2\omega I & B \\
 0 & 0 & 0 & B^T & A - 4\omega I \\
\end{array}
\]

\[
\begin{array}{c|c|c|c}
 A^+ & T^+_{R}U_{1}(R) & \mu^+_{21}(R) & \zeta_2 \\
 & \mu^+_{22}(R) & \zeta_2 & 0 \\
 B^+ & 0 & 0 & 0 \\
\end{array}
\]

**FIG. 7** Structure of the Floquet Hamiltonian for molecular multiphoton dissociation from the ground (\(i = 1\)) to an excited electronic state (\(i = 2\)). The Hamiltonian is composed of diagonal Floquet blocks, of type \(A\), which in turn are composed of two electronic blocks characterized by the kinetic energy operator \(T_R\) and the potential energy curves \(U_i(R)\), \(i = 1, 2\), where \(R\) is the internuclear separation. The rovibrational structure within each electronic block can be discretized by using an appropriate \(L^2\) basis. The rovibronic states are coupled by the electric dipole interaction.

The theory has been applied to the study of direct photodissociation of \(H_2^+\) (1\(\sigma_g^+ - 2\sigma_u^+\)) in both weak and intense fields,\(^2\)\(^9\) and to two-photon dissociation\(^3\)\(^0\) of vibrationally excited \(H_2^+\) (1\(\sigma_g^+, \nu_1 = 6-12\)) (Fig. 8). An independent calculation of (weak-field) two-photon dissociation cross sections \(\sigma_2\) were also performed using the inhomogeneous differential equation (IDE) approach of Dalgarno and Lewis.\(^3\)\(^6\) The two sets of data were found to be in very good agreement. The cross sections \(\sigma_2\) for the low-lying vibrational states are negligibly small but increase rapidly with increasing vibrational quantum number \(\nu_1\), suggesting that experimentally accessible powerful lasers can be used to probe the highly
FIG. 8 Potential-energy curves for the ground electronic state \((1\Sigma_g^+)\) and the first excited electronic state \((2\Pi_u)\) of \(H_2^+\). Also shown is the schematic two-photon dissociation process of \(H_2^+\).

excited vibrational states of the ground electronic state of a homonuclear diatomic molecule.\(37\) The \(H_2^+\) cross sections are largest close to the two-photon dissociation thresh-old and decrease monotonically with increasing photon energy. The pattern is different for HD where the domain features are multiphoton resonant structures.\(38\)

IV. MANY-MODE FLOQUET THEORY

The Floquet approaches we have described require the semiclassical Hamiltonians to be explicitly periodic in time and are therefore applicable to problems involving strictly monochromatic radiation fields. Recently there have been extensive studies of atomic and molecular processes involving the use of two lasers with different frequencies. Examples are: multiphoton double resonance experiments,\(39\)\(a\) collisions in two laser fields,\(39\)\(b\) MPD of polyatomic molecules by two IR lasers,\(39\)\(c\) and multiple quantum transitions in double frequency pulsed NMR experiments.\(39\)\(d\) In addition, a broad class of various phenomena pertaining to nonlinear optics is based on experiments performed with multi-mode laser fields (for a recent review, see Delone et al.\(40\)). Exact treatments of these multi-frequency problems are beyond the scope of conventional Floquet theories.

Most previous semiclassical approaches are based on approximations of one kind or another. The most commonly used approach is the so-called “generalized rotating wave approximation” (GRWA) — an extension of the RWA for the single monochromatic field
case. This approximation takes into account only graphs in which the absorption of a photon of a particular type is accompanied by the subsequent emission of a photon (not necessarily of the same type) and vice versa. The GRWA method is expected to give reasonable results only in some special cases, for example, a two-level system subjected to bichromatic fields with frequencies $\omega_1$ and $\omega_2$ close to the level separation $\omega_0$. For problems involving arbitrary detunings, the GRWA in general cannot be justified and fails to predict many nonlinear features and multiphoton transitions in strong fields.

Recently an exact extension of Shirley's (one-mode) Floquet formalism to a generalized many-mode Floquet theory (MMFT) has been found.\textsuperscript{41,42} This makes it possible to treat the time-dependent problem of any finite-level system exposed to polychromatic fields as an equivalent time-independent infinite-dimensional eigenvalue problem.

Figure 9 shows the structure of the generalized Floquet Hamiltonian, $H_F$, for the case of two monochromatic linearly polarized fields of frequencies $\omega_1$ and $\omega_2$. The $H_F$ has a tridiagonal block as well as a periodic structure in $\omega_2$. Each of the diagonal blocks in $H_F$, namely $A$, in turn also has a tridiagonal (sub-) block and periodic structure in $\omega_1$. The

![Floquet Hamiltonian Structure](image)

**FIG. 9** Floquet Hamiltonian for two radiation-field problems, constructed in a symmetric pattern. $\omega_1$ and $\omega_2$ are the two radiation frequencies and $V^{(i)}_{\alpha\beta}$ $(i = 1, 2)$ are the electric dipole coupling matrix elements for $i$th field. Note that the diagonal block $A$ possesses an identical Floquet structure as that of one laser problem. This can be generalized to the N-field problem.
structure endows the quasi-energy (QE) eigenvalues and quasi-energy state (QES) eigenvectors of $H_F$ with quasi-periodic properties. Once the QE and QES are found from the eigen-analysis, the time-averaged and/or time-dependent multiphoton excitation (MPE) rates can be determined as functions of arbitrary field strengths and photon frequencies.

The MMFT has been applied to the study of the time-evolution of spin-1/2 systems in multi-quantum NMR conditions driven by pulsed linearly polarized bichromatic radio frequency fields.\(^4\)\(^3\) Useful analytical expressions for MPE transition probabilities, bichromatic Bloch-Siegert shifts, and resonance widths, etc., were obtained.\(^4\)\(^3\) We note that experimental studies of the spin dynamics in multi-quantum NMR transitions induced by intense pulsed bichromatic fields is a subject of current interest.\(^4\)\(^4\) More recently, the MMFT has been extended to the study of SU(N) dynamical evolution of N-level systems in polychromatic fields.\(^4\)\(^5\) This is described in the following subsection.

A. SU(N) dynamical symmetries and nonlinear coherence in N-level systems driven by intense polychromatic fields

Multiphoton excitation (MPE) of N-level atomic and molecular systems driven by more than one laser field is a subject of intense current experimental and theoretical interest.\(^5\)\(^6\) In particular, the dynamical evolution of three-level systems in the presence of two strong monochromatic fields has been central to discussions of two-photon NMR on the Spin-1 system,\(^4\)\(^7\) two-photon coherence,\(^4\)\(^8\) coherent population trapping,\(^4\)\(^9\) resonant Raman scattering and double-resonance processes,\(^5\)\(^0\) trilevel echoes,\(^5\)\(^1\) and many others.

It has long been known that for two-level systems, the description of magnetic and optical resonance phenomena can be greatly simplified by the use of the Bloch spin or pseudospin vector.\(^5\)\(^2\) However, extension of the vector description to more complex systems has not been achieved until recently. Hioe and Eberly\(^5\)\(^3\) found that the dynamical evolution of N ($> 3$)–level systems can be expressed in terms of the generalized rotation of an $(N^2 - 1)$ dimensional real coherence vector $\vec{S}$ whose property can be analyzed by appealing to the SU(N) group symmetry. For example, the time-evolution of three-level systems can be described by a coherent vector of constant length rotating in an eight-dimensional space.\(^5\)\(^4\) Furthermore, the existence of a number of unexpected nonlinear constants of motion that govern the density matrix of an N-level system was noticed. In particular, for a three-level system under the two-photon resonance condition, the time-evolution of the eight-dimensional coherent vector $\vec{S}$ can be analyzed in terms of the time evolution of three independent vectors of dimensions three, four, and one, rotating in three disjoint subspaces of those dimensions, provided that the rotating wave approximation (RWA) is valid. The three nonlinear constants of motion in this case correspond to the squares of the lengths of these three subvectors. The dynamical symmetry underlying the three-level system is reminiscent of the Gell-Mann SU(3) symmetry in particle physics. Thus the subspaces of three, four, and one dimension of $\vec{S}$ are analogous to the subspaces of pions ($\Pi^+$, $\Pi^0$, $\Pi^-$), kaons ($K^+$, $K^0$, $\bar{K}^+$, $\bar{K}^0$), and eon ($\eta^0$), respectively. In practice, however, if the laser-atom interactions occur away from the two-photon resonance, or if the RWA is not valid, or if decays are taken into account, then the dynamical subspaces ($8 = 3 + 4 + 1$) dis-
cussed by Hioe and Eberly will no longer be completely independent. The Gell-Mann SU(3) symmetry of the system will then be broken.

The study of SU(N) dynamical evolution of the coherent vector $\vec{S}$ and the symmetry-breaking effects embodied in $N$-level systems subjected to an arbitrary number of monochromatic fields can be greatly facilitated with the use of MMFT. Thus the $(N^2 - 1)$ dimensional coherent vector $\vec{S}(t)$ can be obtained directly from the relation

$$ S_j(t) = \text{Tr} \left[ \rho(t) s_j \right], \quad j = 1, 2, \ldots, (N^2 - 1) $$

where $s_j$ are appropriate SU(N) generators, and the density matrix $\rho(t)$ is determined by

$$ \rho(t) = U(t, t_0) \rho(t_0) U^\dagger(t, t_0). $$

Here $\rho(t_0)$ is the density matrix at the initial time $t_0$ (initial conditions) and the time-evolution operator $U(t, t_0)$ can be determined by the method of MMFT and expressed in terms of quasi-energy eigenvalues and eigenvectors. Furthermore, the generalized Van Vleck (GVV) nearly degenerate perturbation theory can be extended to the analytical treatment of the time-independent many-mode Floquet Hamiltonian. The general idea behind the MMFT-GVV technique is to block-diagonalize the time-independent Floquet Hamiltonian $H_F$ (such as Fig. 9) so that the coupling between the model space and the remainder of the configuration space (called the external space) diminishes to a desired order. The perturbed eigenvalues and eigenvectors corresponding to the set of nearly degenerate states chosen can thus be solved approximately by considering only the model space effective Hamiltonian.

One important feature of the MMFT-GVV approach is that if the perturbed model space wave functions are exact to the nth order, the corresponding quasi-energy eigenvalues in the model space will be accurate to the $(2n + 1)$th order. In that regard, it is interesting to note that the RWA is merely the lowest order (i.e., $n = 0$) limit, namely, model space wave functions correct only to the zeroth order and eigenvalues accurate to the first order. Furthermore, while the RWA can only deal with sequential one-photon processes, the MMFT-GVV approach is capable of treating both one-photon and multiphoton processes on equal footing. Thus the MMFT-GVV approach appears to be a natural and powerful extension beyond the conventional RWA limit for the nonperturbative treatment of multiphoton processes in intense polychromatic fields.

The MMFT-GVV method has been recently applied successfully to a unified treatment of both the SU(3) symmetries and symmetry-breaking effects (caused by non-RWA terms) of three-level systems at two-photon resonances induced by intense bichromatic fields. The MMFT-GVV technique reduces the infinite-dimensional time-independent two-mode Floquet Hamiltonian to a three-by-three (model space) effective Hamiltonian, from which essential analytical properties and vivid geometry of the eight-dimensional coherence vector are revealed for the first time. For a detailed exploitation of this interesting dynamical feature, see Ref. 45.
V. CONCLUSION

In this article we have briefly described some recent developments in semiclassical Floquet theories and their applications to multiphoton excitation, ionization and dissociation processes in intense laser fields. The use and advantages of the Floquet matrix formalism described in this article may be summarized as follows: (1) It is a nonperturbative approach applicable to multiphoton processes involving arbitrary high field strengths. (2) It provides a simple physical picture for the intensity- and time-dependent multiphoton phenomena in terms of avoided crossings of a few real or complex quasi-energy levels. (3) It affords simplicity of numerical computations — it is mainly an eigenvalue problem. (4) In the case of complex quasi-energy formalism, it takes into account self-consistently all the intermediate level shifts and broadenings and multiply coupled continua. Furthermore, only square integrable functions are required and no asymptotic boundary conditions need to be enforced in MPI/MPD calculations.

Other new endeavors in Floquet theoretical developments not discussed in this article include laser-assisted charge-exchange reactions,\textsuperscript{5,7} multi-photon free-free absorptions,\textsuperscript{5,8} and resonant nonlinear optical susceptibilities,\textsuperscript{5,8} etc. Details will be discussed elsewhere.

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