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# Floquet theory and complex quasivibrational energy formalism for intense field molecular photodissociation

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A practical and nonperturbative method is presented for studying molecular photodissociation processes in the presence of (weak or intense) electromagnetic fields, using only square-integrable ( $L^2$ ) functions. By means of the complex coordinate transformation and  $L^2$  discretization of the vibrational continua, the complex quasivibrational energies (QVE) of the Floquet Hamiltonian can be determined by standard non-Hermitian eigenvalue analysis. The real parts of the QVE's provide the ac Stark-shifted vibronic energies, whereas the imaginary parts are related to the photodissociation transition rates. The theory is applied to the direct photodissociation of  $H_2^+(1s\sigma_g - 2p\sigma_u)$  in both weak and strong fields.

## I. INTRODUCTION

There is currently much interest both experimentally and theoretically in the problem of intense field photodissociation of molecules.<sup>1,2</sup> Processes such as direct photodissociation, predissociation, two-photon and multiphoton dissociations are among the ones being studied. At low fields, perturbative technique has been developed,<sup>3</sup> and the theory has been applied successfully to simple model problems. However, there remains the difficulty of how to carry out the summation over the complete vibrational intermediate states correctly. At higher fields, perturbation theory may not be applicable and the picture of dressed molecule or electronic-field surfaces has been introduced and widely used.<sup>2,4</sup>

In this paper we present an alternative practical non-perturbative approach, the complex quasivibrational energy (QVE) formalism, based on the generalization of the conventional finite-level Floquet theory<sup>5</sup> to include the complete set of continuum as well as bound vibronic states. This has the effect of giving each of the dressed vibronic levels an intensity-dependent part (width) in addition to the usual field-induced shifts. Proper interpretation of the frequency and intensity dependence of these complex QVE's gives rise to rates for (multiphoton) photodissociation processes without prior specification of the number of photons involved in the process, and is equivalent to infinite-order perturbation theory, self-consistent in that the shifts and widths of all levels are simultaneously determined.

In Sec. II, the essence of the complex QVE formalism is outlined and a numerical method involving the complex coordinate transformation<sup>6</sup> is suggested for calculating the position of the complex quasivibrational energy state (QVES). The utility and power of this technique will be illustrated in Sec. III by the example of direct photodissociation of  $H_2^+$  in both weak and strong fields.

## II. FLOQUET THEORY AND COMPLEX QUASIVIBRATIONAL ENERGY FORMALISM FOR MOLECULAR PHOTODISSOCIATION

Consider the Schrödinger equation for a molecular system in a (single mode) electromagnetic field,

$$i \hbar \partial \Psi(\mathbf{r}, \mathbf{R}, t) / \partial t = \mathcal{H}(\mathbf{r}, \mathbf{R}, t) \Psi(\mathbf{r}, \mathbf{R}, t), \quad (1)$$

where  $\mathbf{r}$  and  $\mathbf{R}$  stand for electronic and nuclear coordinates respectively, and the semiclassical time-dependent Hamiltonian  $\mathcal{H}$  in the dipole approximation, is given by

$$\mathcal{H}(\mathbf{r}, \mathbf{R}, t) = H(\mathbf{r}, \mathbf{R}) + \boldsymbol{\mu}(\mathbf{r}, \mathbf{R}) \cdot \boldsymbol{\epsilon}_0 \cos \omega t. \quad (2)$$

Here,

$$H(\mathbf{r}, \mathbf{R}) = T_R + H_{e1}(\mathbf{r}, \mathbf{R}) \quad (3)$$

is the field-free total Hamiltonian (with  $T_R$  and  $H_{e1}$  being the nuclear kinetic energy operator and the electronic Hamiltonian respectively),  $\boldsymbol{\mu}(\mathbf{r}, \mathbf{R})$  is the dipole moment operator,  $\boldsymbol{\epsilon}_0$  is the electric field amplitude, and  $\omega$  is the EM frequency. We first seek the solution of the field-free Schrödinger equation,

$$H(\mathbf{r}, \mathbf{R}) \xi_k(\mathbf{r}, \mathbf{R}) = E_k^{(0)} \xi_k(\mathbf{r}, \mathbf{R}). \quad (4)$$

In accordance with the usual assumption of weak coupling of nuclear with electronic motion, one can consider  $R$  as a slowly varying parameter, and the solution of Eq. (4) can be written as

$$\xi_k(\mathbf{r}, \mathbf{R}) = \chi_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}), \quad (5)$$

where  $\chi_k(\mathbf{R})$  and  $\psi_k(\mathbf{r}, \mathbf{R})$  are the nuclear and electronic wave functions, respectively. In the *adiabatic* representation, the electronic wave function  $\psi_k(\mathbf{r}, \mathbf{R})$  is an eigenfunction of  $H_{e1}(\mathbf{r}, \mathbf{R})$  with eigenvalue  $U_k(\mathbf{R})$ , i. e.,

$$H_{e1}(\mathbf{r}, \mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}) = U_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}). \quad (6)$$

We shall assume  $\{\psi_k\}$  forms a complete orthonormal set.

Consider now the solution of Eq. (1) by expanding  $\Psi(\mathbf{r}, \mathbf{R}, t)$  in terms of the field-free basis  $\{\xi_k\}$ ,

$$\begin{aligned} \Psi(\mathbf{r}, \mathbf{R}, t) &= \sum_k a_k(t) \xi_k(\mathbf{r}, \mathbf{R}) \\ &= \sum_k a_k(t) \chi_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}). \end{aligned} \quad (7)$$

Substituting Eq. (7) into Eq. (1), multiplying both sides by  $\xi_j^*(\mathbf{r}, \mathbf{R}) \equiv \chi_j^*(\mathbf{R}) \psi_j^*(\mathbf{r}, \mathbf{R})$  and integrating over  $d\mathbf{r} d\mathbf{R}$ , we find

$$\begin{aligned} i \hbar da_j(t)/dt &= a_j(t) \langle \chi_j(\mathbf{R}) | T_R + U_j(\mathbf{R}) | \chi_j(\mathbf{R}) \rangle \\ &+ \sum_k a_k(t) \langle \chi_j(\mathbf{R}) | \boldsymbol{\mu}_{jk}(\mathbf{R}) \cdot \boldsymbol{\epsilon}_0 | \chi_k(\mathbf{R}) \rangle \cos \omega t, \end{aligned} \quad (j, k = 1, 2, \dots). \quad (8)$$

<sup>a)</sup> Alfred P. Sloan Foundation Fellow.

Here we have assumed that the Born–Oppenheimer approximation is valid, namely, the kinematic coupling terms of nuclear and electronic motions which involve  $\langle \psi_j | T_R | \psi_k \rangle$  can be ignored. In the case of molecular photodissociation, this assumption is equivalent to the Franck–Condon approximation. The electronic transition dipole moment  $\mu_{jk}(\mathbf{R})$  in Eq. (8) is defined to be

$$\mu_{jk}(\mathbf{R}) = \int d\mathbf{r} \psi_j^*(\mathbf{r}, \mathbf{R}) \boldsymbol{\mu}(\mathbf{r}, \mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}). \quad (9)$$

$$i \hbar \frac{d}{dt} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} = \begin{pmatrix} \langle \chi_1(\mathbf{R}) | H_1(\mathbf{R}) | \chi_1(\mathbf{R}) \rangle & 2 \langle \chi_1(\mathbf{R}) | V_{12}(\mathbf{R}) | \chi_2(\mathbf{R}) \rangle \cdot \cos \omega t \\ 2 \langle \chi_2(\mathbf{R}) | V_{21}(\mathbf{R}) | \chi_1(\mathbf{R}) \rangle \cdot \cos \omega t & \langle \chi_2(\mathbf{R}) | H_2(\mathbf{R}) | \chi_2(\mathbf{R}) \rangle \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix}, \quad (10)$$

where

$$H_\alpha(\mathbf{R}) = T_R + U_\alpha(\mathbf{R}), \quad (11)$$

$$V_{\alpha\beta}(\mathbf{R}) = \frac{1}{2} \boldsymbol{\mu}_{\alpha\beta}(\mathbf{R}) \cdot \boldsymbol{\epsilon}_0 \quad (\alpha, \beta = 1, 2). \quad (12)$$

We note that the coupling matrix in Eq. (10) is of two-by-two block form. Each of the electronic blocks specified by the nuclear Hamiltonian  $H_\alpha(\mathbf{R})$  is to be expanded by a manifold of nuclear (i. e., vibrational–rotational) wave functions to be discussed later.

The solution of Eq. (10) is formally equivalent to the solution of the time-dependent Schrödinger equation in matrix form:

$$i \hbar \partial_t \Phi(\mathbf{R}, t) / \partial t = \hat{H}_c(\mathbf{R}, t) \Phi(\mathbf{R}, t), \quad (13)$$

where the time-dependent semiclassical *nuclear* Hamiltonian  $\hat{H}_c$  is defined by

$$[\hat{H}_c(\mathbf{R}, t)]_{\alpha\beta} = H_\alpha(\mathbf{R}) \delta_{\alpha\beta} + 2 V_{\alpha\beta}(\mathbf{R}) \cos \omega t \cdot (1 - \delta_{\alpha\beta}), \quad (\alpha, \beta = 1, 2). \quad (14)$$

Now that  $\hat{H}_c(\mathbf{R}, t) = \hat{H}_c(\mathbf{R}, t + T)$ ,  $T = 2\pi/\omega$ , the Floquet theorem<sup>7</sup> asserts the existence of solutions in the form

$$\Phi_\epsilon(\mathbf{R}, t) = \exp(-i\epsilon t/\hbar) \cdot \eta_\epsilon(\mathbf{R}, t), \quad (15)$$

where  $\Phi_\epsilon$  is called the quasienergy state (QES) corresponding to the quasienergy  $\epsilon$  and  $\eta_\epsilon$  is a periodic function of time, namely,  $\eta_\epsilon(\mathbf{R}, t) = \eta_\epsilon(\mathbf{R}, t + T)$ . The existence of QES in a periodic time-dependent system has been discussed by many authors.<sup>8</sup> Extension of this conventional (real) quasienergy concept to a complex quasienergy formalism, allowing for the coupling of the bound electronic states to the electronic continua, has also been extensively studied recently<sup>9,10</sup> in connection to multiphoton ionization. In the present case of (multi-photon) photodissociation, the quantity of physical interest is the vibronic transition rates from vibrational bound states in one electronic state to the vibrational continua in another electronic state. Appropriate extension of the previous electronic quasienergy formalism<sup>9,10</sup> to vibrational degree of freedom as discussed below leads to a viable method for calculating the complex quasivibrational energies, the imaginary parts of which are directly related to photodissociation rates.

The solution of photodissociation problem, or equivalent

Equation (8) now involves only nuclear degrees of freedom.

Without loss of generality, we consider now in detail the solution of Eq. (8) for the case of two (electronic) states. Since we are concerned with the vibronic transitions between two different electronic states, the contributions due to the diagonal transition dipole moment  $\mu_{jj}(\mathbf{R})$  (which though is crucial for photoabsorption within the single  $j$ th electronic state) will be ignored here. Then the coupled equations in (8) become

lently the solution of Eq. (13) now consists of the following steps. The first step is to transform the dynamical problem described by Eq. (13) into an equivalent static eigenvalue problem.<sup>11</sup> Using the Fourier series expansion for the periodic function in Eq. (15) and for the semiclassical Hamiltonian  $\hat{H}_c(\mathbf{R}, t)$ :

$$\Phi_{\alpha\beta}(\mathbf{R}, t) = \sum_n \phi_{\alpha\beta}^{(n)}(\mathbf{R}) \cdot \exp(in\omega t) \cdot \exp(-i\epsilon_\beta t/\hbar), \quad (16)$$

$$[\hat{H}_c(\mathbf{R}, t)]_{\alpha\beta} = \sum_n H_{\alpha\beta}^{(n)}(\mathbf{R}) \cdot \exp(in\omega t), \quad (17)$$

Eq. (13) then reduces to a matrix eigenvalue equation for the quasienergies  $\epsilon$ 's:

$$\hat{H}_F(\mathbf{R}) \phi(\mathbf{R}) = \epsilon \phi(\mathbf{R}). \quad (18)$$

In Eq. (18), the time-independent Floquet Hamiltonian  $\hat{H}_F$  is an infinite matrix with rows identified by the pair of indices  $\alpha n$ , and columns by  $\beta m$ :

$$(\hat{H}_F)_{\alpha n, \beta m} = [T_R + U_\alpha(\mathbf{R}) + n\hbar\omega] \delta_{\alpha\beta} \delta_{nm} + [\frac{1}{2} \boldsymbol{\mu}_{\alpha\beta}(\mathbf{R}) \cdot \boldsymbol{\epsilon}_0] \delta_{n, m \pm 1} \cdot (1 - \delta_{\alpha\beta}). \quad (19)$$

Here we use Greek letters corresponding to electronic states, while Roman letters will denote Fourier components. We order the components so that  $\alpha$  runs over electronic states before each change in  $n$ . In the case of two electronic states, for example, the Floquet Hamiltonian  $\hat{H}_F$  has the structure shown in Fig. 1. We see  $\hat{H}_F$  has a periodic structure with only the number of  $\omega$ 's in the diagonal elements varying from block to block. The structure endows the eigenvalues and eigenvectors of  $\hat{H}_F$  with periodic properties.

The Floquet matrix so constructed is a real, symmetric matrix and contains no discrete spectrum in the real energy axis. Writing the time evolution operator in the form,

$$\exp(-i\hat{H}_F t/\hbar) = \frac{1}{2\pi i} \int_c dz \exp(-izt/\hbar) (z - \hat{H}_F)^{-1}, \quad (20)$$

gives the usual result<sup>12</sup> that the time dependence is dominated by poles of  $(z - \hat{H}_F)^{-1}$  near the real axis but on higher Riemann sheets, and the complex energies of the poles are related to the positions and widths of the shifted and broadened quasienergy states. These com-

$A+4\omega I$	$B$	$0$	$0$	$0$
$B^T$	$A+2\omega I$	$B$	$0$	$0$
$0$	$B^T$	$A$	$B$	$0$
$0$	$0$	$B^T$	$A-2\omega I$	$B$
$0$	$0$	$0$	$B^T$	$A-4\omega I$

WHERE

$$A = \begin{array}{|c|c|} \hline T_R + U_1(R) & \frac{1}{2} \vec{\mu}_{12}(R) \cdot \vec{\epsilon}_0 \\ \hline \frac{1}{2} \vec{\mu}_{21}(R) \cdot \vec{\epsilon}_0 & T_R + U_2(R) - \omega I \\ \hline \end{array}$$

AND

$$B = \begin{array}{|c|c|} \hline 0 & 0 \\ \hline \frac{1}{2} \vec{\mu}_{12}(R) \cdot \vec{\epsilon}_0 & 0 \\ \hline \end{array}$$

FIG. 1. Structure of the Floquet Hamiltonian. The Hamiltonian is composed of diagonal Floquet blocks, of type A, and off-diagonal blocks of type B.

plex pole positions may be found directly from the analytically continued Floquet Hamiltonian  $\hat{H}_F(\theta)$  obtained by applying the complex coordinate transformation to the nuclear coordinate  $R$ ,  $R \rightarrow R \exp(i\theta)$ . This dilatation transformation effects an analytic continuation of  $(z - \hat{H}_F)^{-1}$  into the lower half-plane on appropriate higher Riemann sheets, allowing the complex quasienergy states (now become square integrable) to be determined by solution of a non-Hermitian eigenvalue problem. In practice, the diagonal electronic blocks  $H_\alpha[R \exp(i\theta)]$  were expanded and discretized by use of appropriate  $L^2$  (square integrable) radial (vibrational) basis. The desired complex quasivibrational energy (QVE) and quasivibrational energy state (QVES) are then identified by the stationary point<sup>6</sup> of the  $\theta$  trajectories of the eigenvalues of  $\hat{H}_F(\theta)$ . Once QVE and QVES are found, the intensity and time-dependent (multiphoton) photodissociation rates can also be determined. In particular, in the weak field limit, a single QVE is sufficient to calculate the one-photon bound-free transition rate. We refer the readers to Ref. 10 for detail discussion on these points.

### III. PHOTODISSOCIATION OF $H_2^+$ —A CASE STUDY

Similar to the complex electronic quasienergy approach<sup>9,10</sup> to atomic multiphoton ionization problems, the power of the QVE approach described in Sec. II lies in its ability to treat both weak and intense field, single and multiphoton photodissociation processes in a unified

nonperturbative fashion. In order to assess the usefulness and accuracy of the QVE method, we first carried out a calculation of the (weak field) single photon vibronic bound-free ( $1s\sigma_g \rightarrow 2p\sigma_u$ ) transition of  $H_2^+$ , for which accurate results have been obtained by others using well established techniques.

For weak-field single-photon two-electronic-state problem, only the minimal ( $2 \times 2$  block) matrix  $A$  shown in Fig. 1 needs to be considered. We shall use the Morse potentials<sup>3</sup>

$$U_i(R) = D_0 \{ \exp[-2\alpha(R - R_e)] - 2t_i \exp[-\alpha(R - R_e)] \}, \quad (i=1, 2) \quad (21)$$

for describing both the ground ( $1s\sigma_g$ ) and the excited repulsive ( $2p\sigma_u$ ) electronic states. For the transition dipole moment we adopt<sup>3</sup>

$$\mu_{12}(R) = \mu(R_e) + \frac{\mu'(R_e)}{\alpha y} \{ 1 - \exp[-\alpha y(R - R_e)] \}, \quad (22)$$

where  $\mu'(R_e)$  is the dipole derivative and  $y$  is the electronic anharmonicity. The molecular parameters used for  $U(R)$  and  $\mu_{12}(R)$  are listed in Table I, which were first suggested by Bunkin and Tugov<sup>3</sup> and used recently also by others.<sup>13</sup> Bunkin and Tugov found that the analytical  $U(R)$  and  $\mu_{12}(R)$  given in Eqs. (21)–(22) are in reasonable agreement with their exact numerical values.<sup>18,19</sup>

For each of the diagonal electronic blocks in matrix  $A$  (Fig. 1), we used the orthonormal harmonic oscillator  $L^2$  basis

$$\chi_P(R) = \left( \frac{\beta}{\pi^{1/2} 2^P P!} \right)^{1/2} H_P(\beta x) \exp(-\frac{1}{2}\beta^2 x^2), \quad (23)$$

to expand the (vibrational) radial wave functions ( $P=1, 2, \dots, N$ ), and  $Y_{Jm_j}(\hat{R})$  to describe the rotational wave function. It is well known<sup>14</sup> that the harmonic oscillator basis provides a compact analytic representation for the complete set of bound and continuum states of an anharmonic oscillator. The harmonic oscillator basis has also been employed successfully by Chu<sup>15</sup> recently for studying the predissociation lifetimes of van der Waals molecules using the method of complex coordinate. In Eq. (23),  $H_P$  is a Hermite polynomial,  $x = R - R_0$  and  $\beta$  is a disposable nonlinear parameter. We used  $R_0 = 3.0a_0$ , and  $\beta = 2.0a_0^{-1}$  ( $a_0 = \text{Bohr radius}$ ), in the case study.

TABLE I. Molecular parameters for  $U_i(R)$  and  $\mu_{12}(R)$ .

Potential <sup>a</sup>	$D_0$ (eV)	$\alpha$ ( $a_0^{-1}$ )	$R_e$ ( $a_0$ )	$t$
$U_1(R)$	2.7925	0.72	2.0	1.0
$U_2(R)$	2.7925	0.72	2.0	-1.11
Trans. dipole moment <sup>b</sup>		$\mu(R_e)$	$\mu'(R_e)$	$y$
$\mu_{12}(R)$		$1.07ea_0$	$0.396e$	-0.055

<sup>a</sup> $U_i(R) = D_0 \{ \exp[-2\alpha(R - R_e)] - 2t_i \exp[-\alpha(R - R_e)] \}$ ,  $i=1$  for  $1s\sigma_g$  and  $i=2$  for  $2p\sigma_u$ .

<sup>b</sup> $\mu_{12}(R) = \mu(R_e) + \frac{\mu'(R_e)}{\alpha y} \{ 1 - \exp[-\alpha y(R - R_e)] \}$ .

The symmetric complex matrix  $A$  of Fig. 1 was diagonalized and the complex QVE's correlated with the photodissociating vibronic levels of the ground electronic state were found. A typical  $\theta$  trajectory of the complex eigenvalue associated with the  $(v=0, j=1)$  level of the  $1s\sigma_g$  state is shown in Fig. 2 for the case of  $N=25$ ,  $\lambda=900$  Å, and  $F_{\text{rms}}=0.001$  a. u. ( $F_{\text{rms}}$  is the rms electric field strength). It is seen the resonance position is clearly identified by the sharp turning point of the  $\theta$  trajectory nearby  $\theta \approx 0.08$  rad. Once the stationary point is located, the (weak-field one-photon) photodissociation cross section may be computed from the imaginary width  $\Gamma [=2 \text{Im}(E)]$  directly,<sup>10</sup>

$$\sigma = \frac{4\pi\omega}{3c} \cdot \frac{\Gamma}{F_{\text{rms}}^2}, \quad (24)$$

where the factor (1/3) comes from rotational angular momentum averaging.

Using Eq. (24), the photodissociation cross sections for the  $(v=0, j=1)$  and  $(v=1, j=1)$  levels of the  $1s\sigma_g$  electronic state were calculated over a range of EM wavelengths and the results are shown in Figs. 3 and 4, respectively. All the data were generated by using  $N=30$ ,  $\beta=2.0a_0^{-1}$ ,  $R_0=3.0a_0$ , and  $\theta=0.08$  rad. The field strength  $F_{\text{rms}}=0.001$  a. u. was chosen because it belongs to the linear,<sup>12</sup> weak field region [i. e.,  $\text{Im}(E) \propto I$  (intensity)  $\propto F_{\text{rms}}^2$ ] for both  $v=0$  and  $v=1$  levels. Convergence with respect to basis set size was also performed. It

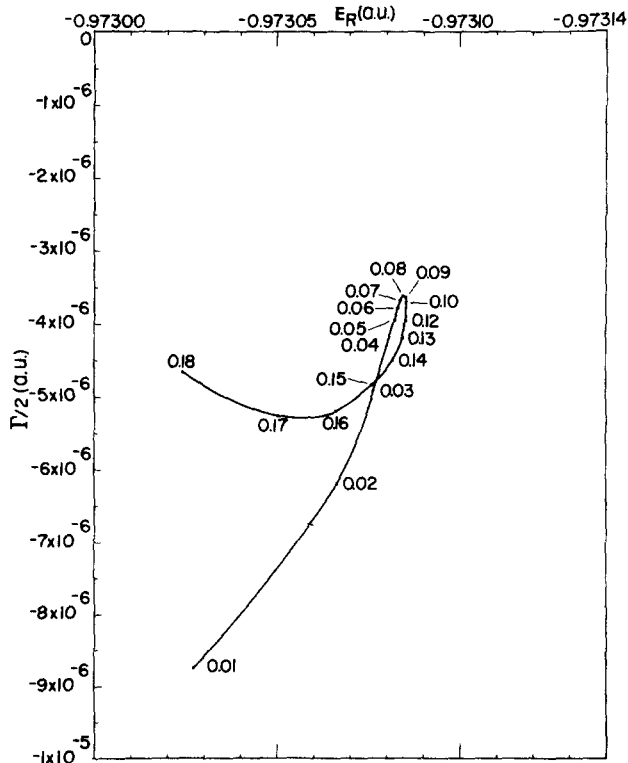


FIG. 2. A typical  $\theta$  trajectory of the complex quasivibrational energy eigenvalue ( $E_R$ ,  $\Gamma/2$ ) associated with the photodissociating level ( $v=0, j=1$ ) of the  $1s\sigma_g$  state of  $\text{H}_2^+$ . The dot (.) numbers shown in the figure are the rotational angles  $\theta$  (in radians). The stationary point nearby  $\theta \approx 0.08$  rad indicates the resonance position sought.

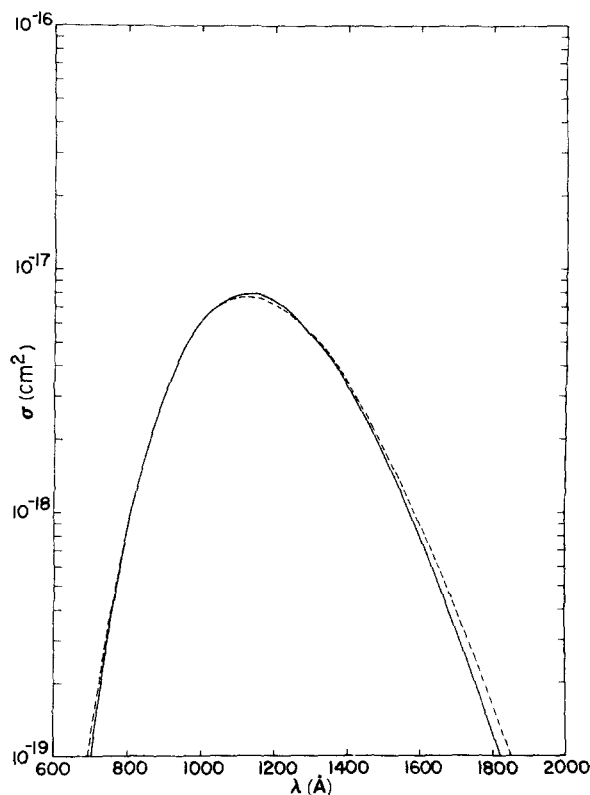


FIG. 3. Weak-field one-photon photodissociation cross sections of  $\text{H}_2^+$  (from the  $1s\sigma_g, v=0, j=1$  level). The solid curve is the result of current QVE calculation whereas the dashed curve is the data of Dunn (Ref. 16).

was found that the data presented in Figs. 3 and 4 have been converged to within 5%. Greater accuracy can be achieved by using larger basis set if desired. In performing the complex eigenvalue analysis, we adopted an

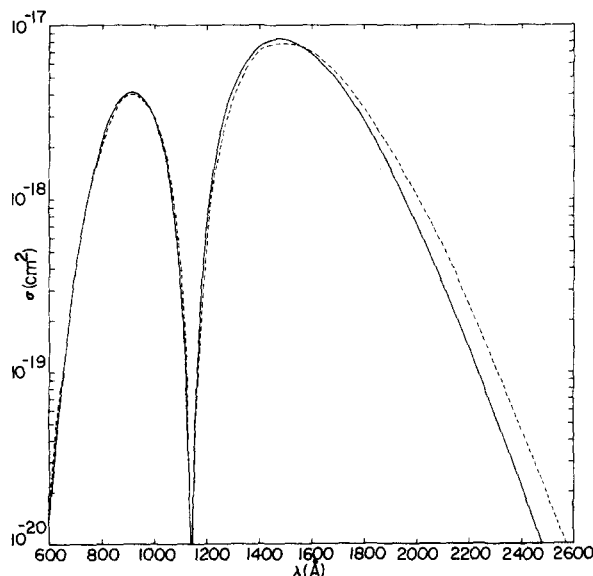


FIG. 4. Weak-field one-photon photodissociation cross sections of  $\text{H}_2^+$  (from the  $1s\sigma_g, v=1, j=1$  level). See the caption of Fig. 3 for curve notation.

inversion iteration technique used before<sup>9,10</sup> which remarkably reduces the amount of computer time. For example, the curves (generated from about 80 data points) presented in both Figs. 3 and 4 took about only 20 mins of computer time in the Honeywell 66/60 system.

Also shown in Figs. 3 and 4 are the data computed by Dunn<sup>16</sup> using the exact numerical data of  $U(R)$ ,<sup>18</sup> and  $\mu_{12}(R)$ <sup>19</sup> and the standard first-order perturbation method. The general agreement between the two sets of data appears satisfactory. The discrepancies in the long wavelength part of curves mainly reflect the difference of potentials and dipole moment used,<sup>17</sup> a fact also pointed out by Bunkin and Tugov.<sup>2</sup> We thus see that the QVE method appears to be capable of providing photodissociation rates of useful accuracy in a straightforward manner.

We now turn to the strong field direct photodissociation of  $H_2^+$ . The field strength  $F_{rms}$  was varied from 0.0001 to 0.02 a. u. It was found that the "generalized" first-order photodissociation cross section<sup>20</sup>  $\sigma(\lambda)$  [computed from Eq. (24)] are essentially invariant up to about  $F_{rms} = 0.005$  a. u. for the main photodissociation bands. However, the cross sections in the long wavelength part ( $\lambda > 1600$  Å) are more susceptible to the change of field strength and  $\sigma(\lambda)$  become field independent only for  $F_{rms} < 0.001$  a. u. In the case of stronger field calculations,

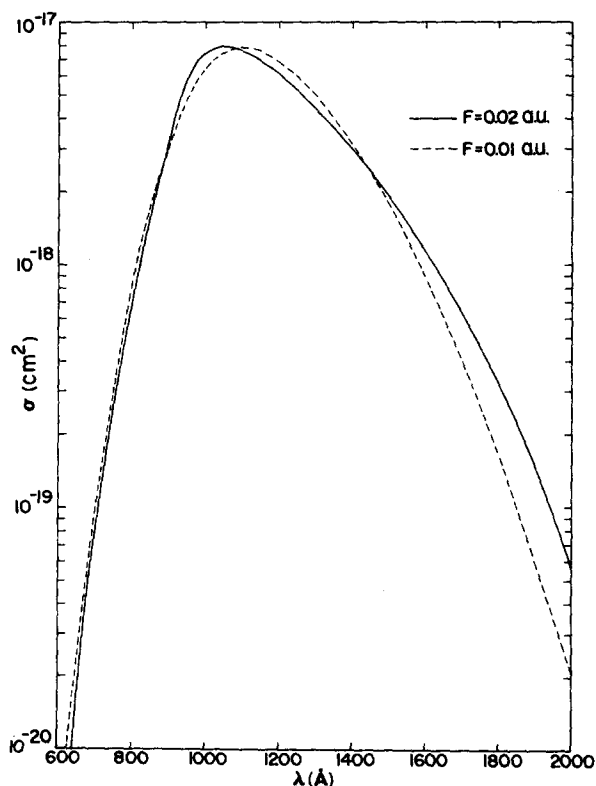


FIG. 5. Strong-field "generalized" one-photon photodissociation cross sections of  $H_2^+$  (from the  $1s\sigma_g$ ,  $v=0$ ,  $j=1$  level). Solid line for  $F_{rms} = 0.02$  a. u., and dashed line for  $F_{rms} = 0.01$  a. u. As discussed in the text, three Floquet blocks (i. e.,  $A$ ,  $A \pm 2\omega I$  in Fig. 1) are required to obtain convergence in strong field calculations. Parameters and basis size used here are  $R_0 = 3.0 a_0$ ,  $\beta = 2.0 a_0^{-1}$ ,  $\theta = 0.08$  rad, and  $N = 30$ .

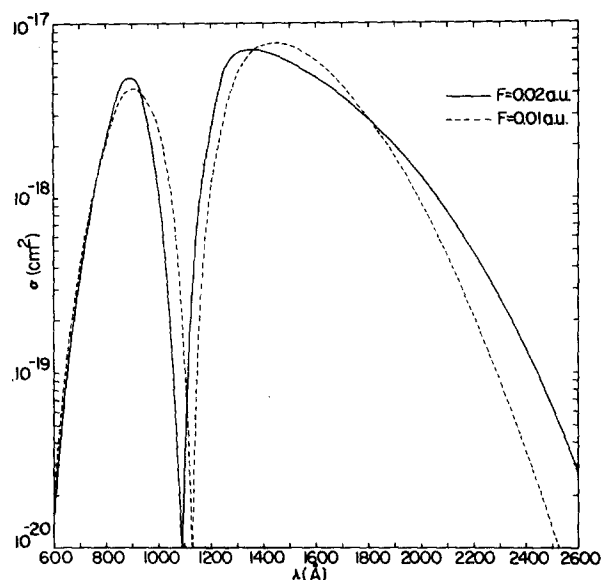


FIG. 6. Strong-field "generalized" one-photon photodissociation cross sections of  $H_2^+$  (from the  $1s\sigma_g$ ,  $v=1$ ,  $j=1$  level). Curve notation same as Fig. 5.

convergence must also be performed with respect to the number of Floquet blocks, as well as with respect to basis size  $N$ . To the extent that enough Floquet blocks are included to obtain convergence, all relevant pro-

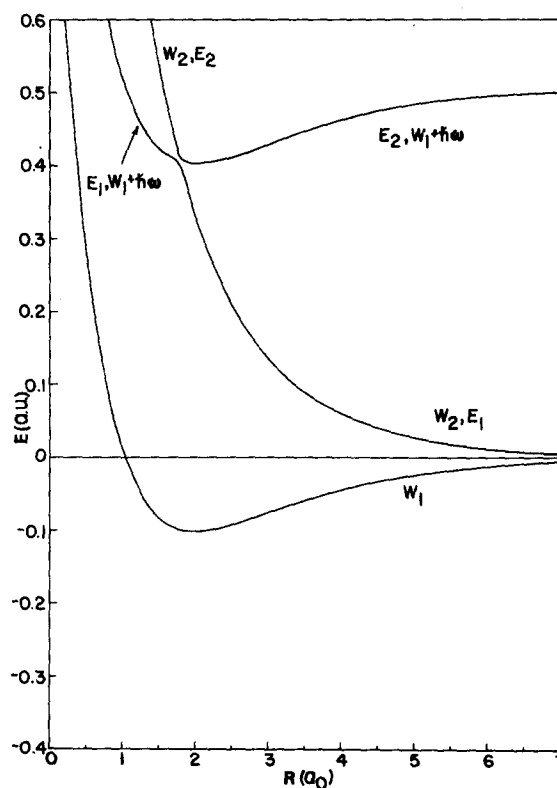


FIG. 7. Electronic-field representation of photodissociation in  $H_2^+$  with field-induced avoided crossing.  $W_1$  and  $W_2$  are, respectively, the field free  $1s\sigma_g$  and  $2p\sigma_u$  adiabatic potentials, whereas  $E_1$  and  $E_2$  are the two electronic-field surfaces corresponding to the single-photon process of interests ( $F_{rms} = 0.001$  a. u.,  $\lambda = 900$  Å).

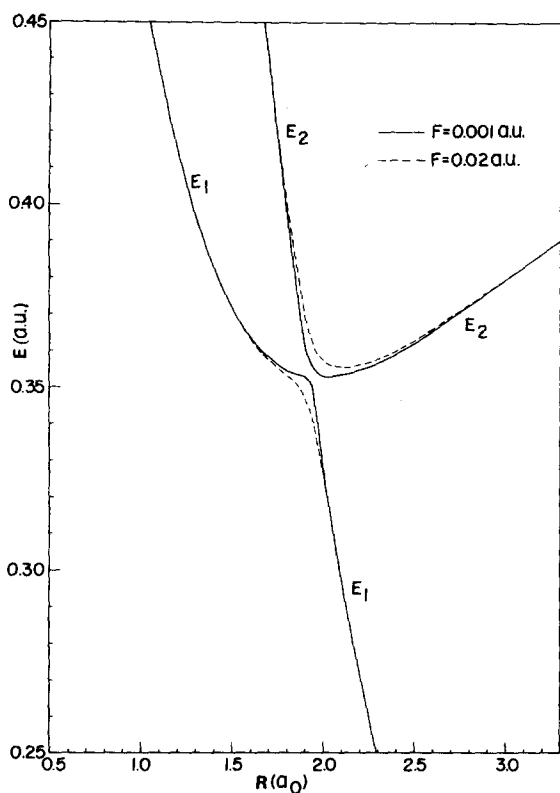


FIG. 8. Field-dependent electronic-field surfaces ( $E_1$ ,  $E_2$ ) nearby the avoided crossing region. Shown are the surfaces for  $\lambda = 1000 \text{ \AA}$  with  $F_{\text{rms}} = 0.001 \text{ a.u.}$  (solid line) and  $F_{\text{rms}} = 0.02 \text{ a.u.}$  (dashed line).

cesses involving different photon numbers are simultaneously and self-consistently included. For example, Figs. 5 and 6 show the intensity dependence of the generalized one-photon dissociation cross sections for the dressed ( $v=0, j=1$ ) and ( $v=1, j=1$ ) quasienergy levels (in the  $1s\sigma_g$  state) as a function of wavelength and field strength. [It was found that three Floquet blocks ( $A + 2\omega 1, A, A - 2\omega 1$ ) are necessary to obtain convergence for the strongest field ( $F_{\text{rms}} = 0.02 \text{ a.u.}$ ) considered in this study.] We see the main photodissociation band(s) appear to be blue shifted (i.e., towards shorter wavelengths) at higher field. Furthermore,  $\sigma(\lambda)$ 's in the longer wavelength part are substantially enhanced as field increases. These flux-dependent phenomena are most easily visualized by considering the electronic-field representation.<sup>2,4</sup> Figure 7 shows the electronic-field surfaces, for the case of  $F_{\text{rms}} = 0.001 \text{ a.u.}$  and  $\lambda = 900 \text{ \AA}$ , computed by the two (electronic) state approximation:

$$E_{1,2}(R) = \frac{1}{2}\{W_1(R) + W_2(R) + \hbar\omega \mp [(W_2(R) - W_1(R) - \hbar\omega)^2 + F_{\text{rms}}^2 \cdot \mu_{12}^2(R)]^{1/2}\},$$

where  $W_1$  and  $W_2$  are the field-free adiabatic potentials for the  $1s\sigma_g$  and  $2p\sigma_u$  states respectively, and  $E_1$  and  $E_2$  are the corresponding adiabatic electronic-field surfaces. As also pointed out by many authors,<sup>2,4</sup> photodissociation process between a bound and a repulsive excited electronic states can be regarded as a (diabatic) curve-crossing or an (adiabatic) avoided-crossing pre-

dissociation problem. Figure 8 depicts the field-dependent electronic-field surfaces  $E_1$  and  $E_2$  nearby the susceptible avoided-crossing region for the cases of  $\lambda = 1000 \text{ \AA}$  and  $F_{\text{rms}} = 0.001$  and  $0.02 \text{ a.u.}$  It is seen that the two electronic-field surfaces "repel" each other as field increases, which in turn affects the photodissociation transition probabilities.

In summary, we have shown in this paper that the complex QVE formalism provides an alternative, in the case of weak field, and a practical nonperturbative, in the case of strong field, method for studying photodissociation processes. Interesting and useful extensions of the QVE method include multiphoton dissociation of small molecules in intense fields and bound-free transition involving shape resonances in the upper electronic state,<sup>21</sup> etc. Research projects along these directions are underway.

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- <sup>1</sup>N. Bloembergen and E. Yablonovitch, *Phys. Today* **31**, (No. 5), 23 (1978), and references therein.
- <sup>2</sup>See, for example, J.-M. Yuan and T. F. George, *J. Chem. Phys.* **68**, 3040 (1978); A. M. F. Lau, *Phys. Rev.* **13**, 139 (1976); A. D. Bandrauk and M. L. Sink, *J. Chem. Phys.* **74**, 1110 (1981).
- <sup>3</sup>See, for example, F. V. Bunkin and I. I. Tugov, *Phys. Rev. A* **8**, 601 (1973).
- <sup>4</sup>T. F. George, I. H. Zimmerman, J.-M. Yuan, J. R. Laing, and P. L. DeVries, *Acc. Chem. Res.* **10**, 449 (1977), and references therein.
- <sup>5</sup>D. R. Dion and J. O. Hirschfelder, *Adv. Chem. Phys.* **35**, 265 (1976); S. Autler and C. H. Townes, *Phys. Rev.* **100**, 703 (1955); C. Cohen-Tannoudji and S. Haroche, *J. Phys. (Paris)* **30**, 125, 153 (1969); J. H. Shirley, *Phys. Rev. B* **138**, 979 (1965).
- <sup>6</sup>See, for example, in Proceedings of the 1977 Sanibel Workshop on Complex Scaling, *Int. J. Quantum Chem.* **14**, No. 4 (1978).
- <sup>7</sup>G. Floquet, *Ann. de l'Ecole Norm. Suppl.* **12**, 47 (1883).
- <sup>8</sup>R. H. Young, W. J. Deal Jr., and N. R. Kestner, *Mol. Phys.* **17**, 369 (1969); Ya. Zel'dovich, *Sov. Phys. Usp.* **16**, 427 (1973); H. Sambe, *Phys. Rev. A* **7**, 2203 (1973); W. R. Salzman, *Phys. Rev. A* **10**, 461 (1974); J. M. Okuniewicz, *J. Math. Phys.* **15**, 1587 (1974).
- <sup>9</sup>S.-I. Chu and W. P. Reinhardt, *Phys. Rev. Lett.* **39**, 1195 (1977); S.-I. Chu and W. P. Reinhardt, in *Multiphoton Processes*, edited by J. Eberly and P. Lambropoulos (Wiley, New York, 1978), pp. 171-178.
- <sup>10</sup>S.-I. Chu, *Chem. Phys. Lett.* **54**, 367 (1978); **58**, 462 (1978); **64**, 178 (1979).
- <sup>11</sup>J. H. Shirley, *Phys. Rev. B* **138**, 979 (1965).
- <sup>12</sup>P. Lambropoulos, *Adv. At. Mol. Phys.* **12**, 87 (1976).
- <sup>13</sup>See, for example, A. Lami and N. K. Rahman, *Chem. Phys. Lett.* **71**, 353 (1980).
- <sup>14</sup>C. S. Lin and G. W. F. Drake, *Chem. Phys. Lett.* **16**, 35 (1972).

<sup>15</sup>S.-I. Chu, *J. Chem. Phys.* **72**, 4772 (1980).

<sup>16</sup>G. H. Dunn, *Phys. Rev.* **172**, 1 (1968).

<sup>17</sup>The reason of adopting analytical forms of  $U(R)$  and  $\mu_{12}(R)$ , besides its simplicity and usefulness, is due to the fact that complex coordinate transformation (Ref. 6) is known only applicable to analytic functions. The possibility of extending complex coordinate transformation to numerical potentials is being investigated in our laboratory.

<sup>18</sup>D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. R. Soc. London Ser. A* **246**, 215 (1953).

<sup>19</sup>D. R. Bates, *J. Chem. Phys.* **19**, 1122 (1951).

<sup>20</sup>Equation (24) is applicable only to the weak field, linear optical region. Nonlinear optical effects occur at stronger fields.

<sup>21</sup>See, for example, T. Uzer and A. Dalgarno, *Chem. Phys. Lett.* **63**, 22 (1979).