# Floquet analysis of the far-infrared dissociation of a Morse oscillator

John J. Tanner* and M. Matti Maricq†
*Department of Chemistry, Brown University, Providence, Rhode Island 02912*
(Received 10 April 1989)

The dynamics of a highly excited Morse oscillator in an intense laser field are examined using Floquet theory. Two classes of quasienergy states are found, broad states, which extend over a wide range of the Morse basis, and narrow states, which are localized to a small number of Morse states. A comparison to a quantum simulation of the dissociation dynamics via the fast-Fourier-transform grid method reveals that the projection of the initial oscillator state onto the broad states leads to dissociation, whereas the projection onto narrow states implies localization of the oscillator. The Floquet analysis explains a number of observations from the simulation including the slowdown of the dissociation rate and concomitant localization of the oscillator, the threshold dependence of dissociation on field intensity, and the variation in dissociation probability with field frequency and initial oscillator state.

## I. INTRODUCTION

There recently has been growing interest in examining how simple physical systems respond to intense electromagnetic radiation. This includes the microwave ionization of hydrogen atoms, the periodically kicked rotor, and the dissociation of a Morse oscillator. The emphasis has been on contrasting the predictions of classical and quantum mechanics. A principal concern is the question of how stochasticity is manifested in quantum mechanics, a question that pertains to a variety of problems including intramolecular energy transfer,[1-3] Rydberg atoms in strong magnetic fields,[4] and a number of model systems.[5-11]

A particularly well-studied model system is the periodically kicked rotor.[12-19] A classical description of this system finds the energy of the rotor to grow diffusively and without limit for sufficiently strong kicks. Subsequently, Hogg and Huberman[20] showed that, in contrast, the energy of the quantum-mechanical rotor is quasiperiodic and remains bounded. Considerable insight into the dynamics was shed by Fishman and co-workers[17-19] when they showed the kicked rotor to be analogous to Anderson localization[21,22] of an electron in a disordered lattice. Thus, in this system, quantum mechanics imposes recurrent, localized behavior while preventing stochastic behavior.

In their classical description of microwave ionization of hydrogen,[23-29] Jensen[30] and Leopold and co-workers[31,3] argue that ionization occurs by stochastic diffusion of the electron in phase space, a situation that by the Kolmogorov-Arnold-Moser theorem[33] is allowed only above a critical value of the microwave field. In contrast, numerical solution of the Schrödinger equation by Casati and co-workers[34-36] reveals localization of the electron for field strengths below the so-called delocalization border, even though the classical system exhibits stochasticity at the same field strength. Above the border the wave function becomes delocalized, and the energy growth of the system is diffusive as in the classical case.

Blümel and Smilansky[37,38] have adopted a different approach to the microwave ionization problem. They propose a two-step process, with ionization occurring through high-lying atomic states in an ionization window, which couple efficiently to the continuum. They interpret, using a Floquet analysis, that excitation of the initial state into the window region occurs via broad quasienergy states. Thus, while the classical description[30-32] of the microwave ionization of hydrogen involves a transition from regular to chaotic behavior, the quantum-mechanical picture[37,38] is one of a transition from narrow to broad states.

Classical studies of the Morse oscillator also reveal that dissociation proceeds via chaotic trajectories.[39] However, Walker and Preston[40] and Goggin and Milonni[41] find that the quantal and classical evolution of oscillator position and energy agree only for a short time when the oscillator is exposed to an intense field. The latter authors provide estimates, based on a quantal extension of the resonance overlap criterion,[42] for the critical field necessary for dissociation. In contrast, Heather and Metiu[43,44] have taken an entirely different point of view and examined the momentum distribution of the fragments from $H_2$ dissociation. While illuminating, the focus of the previous work has been on the interactions of nearly resonant light with HF and $H_2$, molecules which support a relatively small number of bound states. We are interested in a situation that is more analogous with the microwave ionization of hydrogen. Therefore, we chose a Morse oscillator with 179 bound states and examine the dissociation of the oscillator from a highly excited initial state under conditions that require 100–200 photons to be absorbed.

In a previous paper[45] we reported a quantum-mechanical simulation of the dissociation of a highly excited Morse oscillator by an intense laser field. Above a threshold field intensity, we found that there is initially a rapid flow of oscillator probability into the continuum; however, the dissociation rate subsequently slows because

 ©1989 The American Physical Society

the remaining bound portion of the wave function is localized to a relatively narrow range of Morse eigenstates. This may be related to the observation by Brown and Wyatt[46] that the existence of cantori in classically stochastic regions of phase space poses a barrier to quantum wave-packet evolution. The purpose of the present paper is to see what light a Floquet viewpoint, similar in spirit to Blümel and Smilansky's,[37,38] can shed on the dissociation dynamics. We find that the quasienergy states fall into two distinct classes, narrow states that overlap with a local distribution of Morse states and broad states that overlap with the entire range of Morse states above a threshold quantum number. The observations from the simulation can be explained by assuming that the broad component of the initial oscillator state couples rapidly to the dissociation continuum, whereas the narrow component remains localized to a small group of bound states.

In Sec. II we present the Hamiltonian for the Morse oscillator interacting with a classical electromagnetic field and our method of determining the Floquet states of this system. Section III describes the structure and widths of the quasienergy eigenstates. In Sec. IV we compare the results of the Floquet analysis with the quantum simulation of the dissociation dynamics. In particular, we interpret in terms of the quasienergy states the threshold in laser intensity required to achieve dissociation, the variation in dissociation probability as a function of laser frequency, and the variation with respect to initial oscillator state.

## II. FLOQUET ANALYSIS

The objective of this paper is to provide insight into the dissociation dynamics of a Morse oscillator in an intense laser field. We approach this task by comparing the results obtained from a Floquet analysis of the interaction between a quantized oscillator and a classical electromagnetic field with the exact dissociation dynamics obtained from the quantum-mechanical simulation reported in Ref. 45. This section presents the Hamiltonian of the system, briefly reviews the Trotter product formulation[47–49] of the simulation, and describes the Floquet analysis.

### A. Hamiltonian

A semiclassical description of the interaction between a Morse oscillator and a single-mode radiation field is provided by the periodically time-dependent Hamiltonian

$$\begin{aligned}\mathcal{H}(t)&=T+V_0+V_1(t)\\&=\hat{\mathbf{p}}^2/(2m)+V_0(\hat{\mathbf{z}}-z_{\mathrm{eq}})+\hat{\boldsymbol{\mu}}\cdot F\sin(\omega t)\ ,\end{aligned}\tag{1}$$

where $\hat{\mathbf{p}}$, $\hat{\mathbf{z}}$, and $\hat{\boldsymbol{\mu}}$ are momentum, position, and dipole moment operators, respectively. The Morse potential has the form

$$V_0(x)=D_0(e^{-2\alpha x}-2e^{-\alpha x})\ ,\tag{2}$$

with a dissociation energy $D_0$, fundamental vibrational frequency $\omega_e=\alpha(2D_0/m)^{1/2}$, and an anharmonicity of $\omega_e x_e=\omega_e^2/4D_0$. The interaction between the oscillator and radiation of intensity $F$ takes place within the dipole approximation. This assumes that the dominant interaction occurs with the dipole moment of the oscillator, which we arbitrarily choose to be

$$\hat{\boldsymbol{\mu}}=\hat{\mathbf{z}}\exp(-\hat{\mathbf{z}}/0.375z_{\mathrm{eq}})\ .\tag{3}$$

This form has been used successfully in previous dissociation studies[41,43,44] to represent the dipole moment of a diatomic molecule. Variation of the position of the maximum of this function does not change the qualitative features of the dissociation. Interaction occurring via higher-order electric moments or via magnetic moments are much weaker and therefore not incorporated into the present discussion.

In this study we choose a Morse oscillator consistent with the spectroscopic constants of the $I_2^+$ molecule[50] (note that our intention is not to describe the dynamics of the $I_2^+$ ion; we merely employ its molecular constants in our model). This choice is made in order to facilitate a comparison of the present work with the microwave ionization of hydrogen atoms.[23–32,34–38] The unperturbed molecule has a vibrational frequency $\omega_e=240\ \mathrm{cm}^{-1}$, an anharmonicity of $\omega_e x_e=0.665\ \mathrm{cm}^{-1}$, and a dissociation energy $D_0=2.683$ eV. Therefore, the oscillator supports 179 bound states. Of particular interest is the evolution of the oscillator from a state of high initial excitation (e.g., $n_0=50$) when it is subject to an intense field having a frequency that is a fraction ($\simeq 30$–$40\%$) of the energy spacing between the initial state and its immediate neighbors. Such a situation is realized for the excited states ($n>30$) for $I_2^+$ when the frequency of the field is approximately $\omega=60\ \mathrm{cm}^{-1}$. In this case 2–3 photons are need-

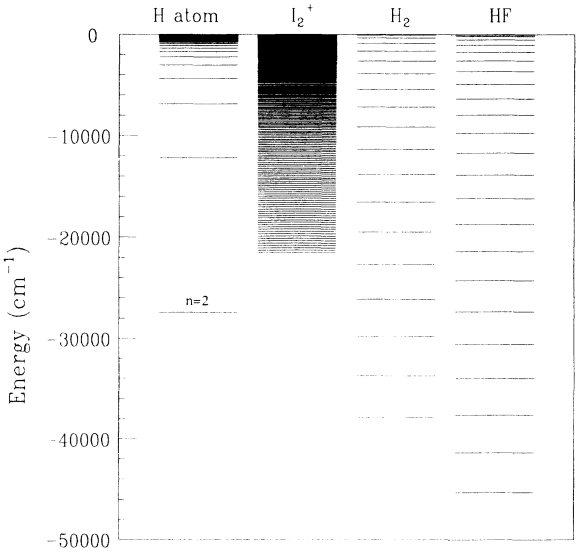


FIG. 1. Comparison of the energy-level diagrams for the hydrogen atom (beginning at $n=2$), the Morse oscillator of this study, $I_2^+$, and two previously studied oscillators.

TABLE I. Comparison of the number of photons needed to excite and dissociate $I_2^+$ vs excite and ionize hydrogen.

| | Far-infrared dissociation[a] of $I_2^+$ Number of photons for | | Microwave ionization[b] of H Number of photons for | |
|---|---|---|---|---|
| $n_0$ | Excitation to $n+1$ | Dissociation | Excitation to $n+1$ | Ionization |
| 40 | 3.1 | 219 | 11 | 229 |
| 50 | 2.9 | 187 | 5.7 | 146 |
| 60 | 2.7 | 161 | 3.3 | 102 |
| 100 | 1.8 | 72 | 0.73 | 37 |

[a] $\omega = 60\ \text{cm}^{-1}$.
[b] $\omega = 0.3\ \text{cm}^{-1}$.

ed to excite the oscillator to the next higher quantum state and roughly 100–200 photons must be absorbed to reach the dissociation continuum. Table I compares these numbers to the number of photons required to excite and ionize a hydrogen atom using a microwave frequency of 0.3 $\text{cm}^{-1}$. Based on this comparison, one might expect the far-infrared dissociation from $n_0 = 50$ to resemble the microwave ionization of $n_0 = 50$ or $n_0 = 60$, and, indeed, this is found to be the case.

Figure 1 gives an idea of how the energy level spacing of $I_2^+$ compares with that of previously studied Morse oscillators[39–41,43,44] representing $H_2$ and HF molecules, and to that of the hydrogen atom. Note the rapid decrease in atomic energy level spacings relative to that of the oscillator levels. The energy level spacing in the hydrogen atom varies as $27.212\ \text{eV}/n^3$ (for large $n$) while the spacing of the Morse oscillator decreases more slowly as $\Delta E(n) = \omega_e - 2n\omega_e x_e$ (for large $n$).

### B. Floquet Hamiltonian

The Hamiltonian describing a quantum-mechanical Morse oscillator in a single-mode classical electromagnetic field is periodically dependent on time, with period $\tau = 2\pi/\omega$. This "symmetry" in time implies that there exists a unitary period-advance mapping[51],

$$U(\tau,0) = e^{-iH_F\tau} \tag{4}$$

that propagates the system over one period of time. Note that the Floquet Hamiltonian $H_F$ does not itself depend on time. Therefore, upon *striboscopic* observation at times $N_\tau$,

$$|n_0(N\tau)\rangle = \exp(-iH_F N\tau)|n_0(0)\rangle$$

and the system appears to evolve under a conservative Hamiltonian. As a consequence, the eigenvalues and eigenvectors of the Floquet Hamiltonian contain the essential dynamical information of the system. We denote the quasienergy, or Floquet, states by $|\alpha\rangle$ and energies by $E_\alpha$. Because the period advance mapping is defined with respect to a finite time $\tau$ the quasienergies are only defined modulo $2\pi/\tau$.

The usefulness of the Floquet states arises in the following way. Consider the projection onto the unperturbed Morse oscillator eigenstates $|m\rangle$ of the initial state $|n_0\rangle$ after it has evolved for $N$ cycles of the field

$$\langle m|n_0(N\tau)\rangle = \langle m|U(\tau)^N|n_0(0)\rangle \ .$$

By inserting the completeness of the quasienergy states on the right-hand side, we obtain

$$\langle m|n_0(N\tau)\rangle = \sum_\alpha \exp(-iE_\alpha N\tau)\langle m|\alpha\rangle\langle\alpha|n_0(0)\rangle \ . \tag{5}$$

Thus, excitation from an initial state $|n_0\rangle$ to a state $|m\rangle$ is possible only if at least one quasienergy state overlaps both oscillator states. Note that this statement is *independent* of the time one allows the system to evolve; the time dependence enters through the exponential phase factors in Eq. (5). Extensive excitation of the oscillator, such as is necessary for dissociation, can only occur if there exist *broad* Floquet states, states that have significant overlap with a large number of Morse eigenstates. *Narrow* Floquet states, on the other hand, lead to localization of the initial state to a relatively small number of Morse eigenstates. A third possibility, namely, that a quasienergy state overlaps with two widely spaced groups of Morse eigenstates (i.e., the state $|\alpha\rangle$ has a bimodal distribution), is not observed.

Except for special cases, such as the harmonic oscillator,[52] an exact determination of the Floquet Hamiltonian is not possible. Perturbation methods, such as the average Hamiltonian method,[53,54] are suspect because of the high laser intensity considered in this study. We choose to determine $H_F$ numerically; however, we truncate the Morse oscillator state space to include only bound states. Blümel and Smilansky[37,38] take a similar approach in their treatment of the microwave ionization of hydrogen. Continuum states can be included in a discretized manner by placing the oscillator into a one-dimensional box having a length sufficiently larger than the outer turning points for the high-lying oscillator states.[46]

The Floquet Hamiltonian is determined by calculating numerically the period-advance propagator. This proceeds by partitioning the evolution operator

$$U(t) = U(t,t-\Delta t)\cdots U(2\Delta t,\Delta t)U(\Delta t,0) \tag{6}$$

into a product of short-time propagators. The time increment $\Delta t$ is chosen sufficiently short to allow the propaga-

tor in each time slice to be integrated under the assumption that $\mathcal{H}(t)$ is approximately constant *and* to allow the expansion

$$U(t,t-\Delta t)=\exp(-i\mathcal{H}_0\Delta t/2)\exp[-iV_1(\hat{\mathbf{z}},t)\Delta t]\times\exp(-i\mathcal{H}_0\Delta t/2)\ . \quad (7)$$

Typically, a time increment of $\tau/50$ is sufficiently short to yield convergent results. Each of the operators $\mathcal{H}_0$ and $V_1(\hat{\mathbf{z}},t)$, is expressed in a basis of bound Morse oscillator states. The former is diagonal in this basis, and its exponentiation is straightforward. The dipole moment operator in $V_1$, however, is not diagonal in the Morse basis. It is exponentiated via

$$\exp[-iV_1(\hat{\mathbf{z}},t)\Delta t]=A^{\dagger}\cdot\exp[-iA\cdot\hat{\mathbf{u}}\cdot A^{\dagger}F\sin(\omega t)\Delta t]\cdot A\ ,$$

where $A$ diagonalizes the dipole moment operator of Eq. (3). Note that the diagonalization need only be carried out once and matrix $A$ stored by the computer. The short-time propagators, determined for each time slice via Eq. (7), are then concatenated by matrix multiplication to form $U(\tau)$. Finally, the period-advance operator is itself diagonalized to find the Floquet states $|\alpha\rangle$ and the quasienergies $E_\alpha=(i/\tau)\ln[\mathrm{diag}U(\tau)]$.

The Floquet analysis that we present for the Morse oscillator dissociation omits the continuum and one may well ask what light such an analysis can shine on the problem. We show below by comparing the Floquet analysis to an exact quantum simulation, which does include the continuum, that it provides considerable insight. Dissociation can only occur after extensive dynamics within the bound-state space leading to excitation of bound states near the dissociation continuum. Actual dissociation then occurs in a "second" step via transitions from these states to the continuum states. Our results suggest that it is the initial excitation process that plays the key role in determining how the dissociation probability changes as a function of initial oscillator state, laser intensity, and laser frequency.

### C. Quantum simulation

A numerically exact simulation of the evolution of an initial state $|n_0\rangle$, to which the Floquet results are compared, is achieved by the fast-Fourier-transform (FFT) grid method.[47,48,55] The propagator is partitioned in time as per Eq. (6). In the FFT grid method, however, the time increment $\Delta t$ is chosen short enough that $\mathcal{H}(t)$ is approximately constant over the time increment *and* sufficiently short to allow use of the Trotter product formula[49]

$$U(t,t-\Delta t)=\exp(-iT\Delta t/2)\exp[-iV(\hat{\mathbf{z}},t)\Delta t]\times\exp(-iT\Delta t/2)\ , \quad (8)$$

where $V(\hat{\mathbf{z}},t)=V_0(\hat{\mathbf{z}})+V_1(\hat{\mathbf{z}},t)$. By using the symmetric form[47] of Eq. (8), which divides the kinetic-energy term into two parts, one obtains an expression accurate to $O(\Delta t^3)$ as opposed to $O(\Delta t^2)$ for the usual form of the Trotter product. It is the separation of the kinetic- and potential-energy terms in Eq. (8) that places the more severe restriction on the length of $\Delta t$. Typically we set it equal to $\frac{1}{100}$ of the period of the oscillator, or $\Delta t\simeq 2$ fs.

A calculation of the evolution of an initial state $|n_0\rangle$ proceeds as follows. The state $|n_0\rangle$ is expanded in a basis of momentum eigenstates and multiplied by the right-hand kinetic-energy propagator of Eq. (8). The result is inverse Fourier transformed into position space and multiplied by the potential-energy propagator. Fourier transformation back into momentum space and multiplication by the remaining kinetic-energy propagator completes the evolution over one time increment $\Delta t$. Repeating this sequence of steps $N$ times yields a quantum-mechanical simulation of the Morse oscillator dynamics over a time $t=N\Delta t$.

The numerical implementation of the Fourier-transform method requires discretization of both position and momentum space in addition to the time grid introduced above. The initial wave function is typically placed in a 2048-element complex array with a spacing of $\Delta x=0.01a_0$ and extends from $x_{\min}=-4a_0$ to $x_{\max}\simeq 16a_0$. The corresponding momentum-space grid has $\Delta k=2\pi/(x_{\max}-x_{\min})$ and $k_{\max}=\pi/\Delta x$.

A principal advantage of the FFT grid method is that it includes the continuum states of the Morse oscillator in a natural way. It, thereafter, allows us to simulate the dissociation dynamics. The amount of dissociation that takes place from an initial state $|n_0\rangle$ after at time $t$ is given by

$$P_{\mathrm{dis}}(t)=1-\sum_n|\langle n|n_0(t)\rangle|^2\ , \quad (9)$$

where the summation extends over all bound states of the oscillator. A simpler procedure, which we find to work well, is to determine the probability of dissociation from

$$P_{\mathrm{dis}}(t)=\int_{x_c}^{\infty}dx\,|\langle x|\psi(t)\rangle|^2\ , \quad (10)$$

where $x_c$ is typically set to $10a_0$. The right-hand turning points of the bound states lie at smaller distances; therefore $P_{\mathrm{dis}}(t)$ is not sensitive to the precise choice of $x_c$. The reader will find a more complete description of the FFT grid method and its use to study the dissociation of the Morse oscillator in Refs. 44 and 45.

Both the Floquet analysis and the FFT grid method require knowledge of Morse oscillator wave functions $\psi_n(x)$ for highly excited states (up to $n=179$). For the Floquet analysis they are needed to compute matrix element of the dipole moment operator; for the quantum simulation, they provide the expansion coefficients of the initial state in the basis of position eigenstates. These wave functions are known analytically in terms of hypergeometric functions; however, numerical evaluation of the high-order ($>20$) wave functions in this way is difficult because of errors due to finite precision. Instead, we solve numerically the Schrödinger equation, $\mathcal{H}_0\psi_n(x)=E_n\psi_n(x)$, using the Sams and Kouri method[56] and the known Morse oscillator eigenvalues, $E_n=\omega_e(n+\frac{1}{2})-\omega_e x_e(n+\frac{1}{2})^2$. The solution is propagated in increments of $0.001a_0$ from $x=-1.2a_0$ until $0.1a_0$ beyond the right-hand classical turning point, at which point a Wentzel-Kramers-Brillouin (WKB) solution is

used. As a safeguard the number of nodes is counted and the solution is rejected if this number does not equal $n$.

## III. QUASIENERGY STATES

The Floquet Hamiltonian contains the essential dynamical information for a periodically time-dependent system; in a stroboscopic sense it is a constant of the motion for the system. How the quasienergy states change as a function of the frequency and intensity of the radiation should reflect the manner in which the dynamics of the Morse oscillator change with these parameters. When the laser intensity is zero the quasienergy eigenstates are identical to the Morse oscillator states. Figure 2 illustrates the situation for relatively low intensity radiation, $F=0.019$ Hartree/$a_0$, having a frequency of $\omega=60$ cm$^{-1}$. It shows the expansion coefficients (squared) for a series of quasienergy state in the basis of bound Morse eigenstates, or, equivalently, the expansion coefficients (squared) for the Morse eigenstates in a basis of quasienergy states. At low intensity radiation there remains a nearly one to one correspondence between a large number of Morse and Floquet eigenstates. Note that these *narrow* Floquet states correspond to low excitation of the oscillator ($n<70$). As the excitation increases, the quasienergy states broaden and develop structure ($70<\alpha<120$). At the highest excitations ($\alpha>120$) the quasienergy states begin to overlap with a *broad* range of Morse states. In comparing the Floquet analysis to the quantum simulation reported in Ref. 45, we are particularly interested in the fate of the initial state $n_0=50$. Note that at this field intensity it overlaps only with narrow Floquet states. Accordingly, by Eq. (5) it has little chance of dissociating. This is confirmed by the simulation.

When the intensity of radiation is increased to $F=0.136$ hartree/$a_0$, the situation changes dramatically. As Fig. 3 shows, there is a marked distinction between broad and narrow Floquet states. The increase in field intensity has caused the region of broad states to grow extensively. At this intensity there is an abrupt transition between these two classes of Floquet states at approximately $n=55$, or, equivalently, $\alpha=55$. Quasienergy states for $\alpha<55$ each overlap only with a local distribution of Morse states. This suggests that it is possible to define a *localization length* for the perturbed oscillator based on the width of this distribution. Above the threshold state, the quasienergy states overlap with the entire range of Morse states above $n=55$. There is no reason to believe that this overlap would not extend to the continuum states were they included in the Floquet analysis. At this field intensity, the initial state $n_0=50$ shows some overlap with the broad quasienergy states, in addition to its overlap with the narrow states. This implies that at $F=0.136$ hartree/$a_0$ $n_0=50$ should begin to dissociate. Further increase in the field intensity leads to even larger regions of broad quasienergy states implying that dissociation of $n_0=50$ becomes progressively more efficient.

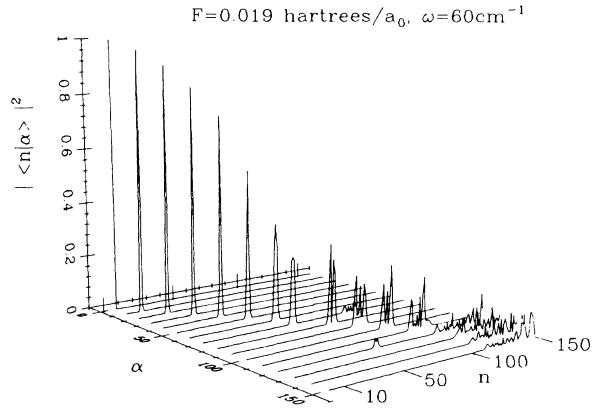


FIG. 2. The quasienergy eigenstates for a "low" intensity field. For reference, the field frequency is approximately $\frac{1}{4}$ the fundamental frequency of the oscillator.

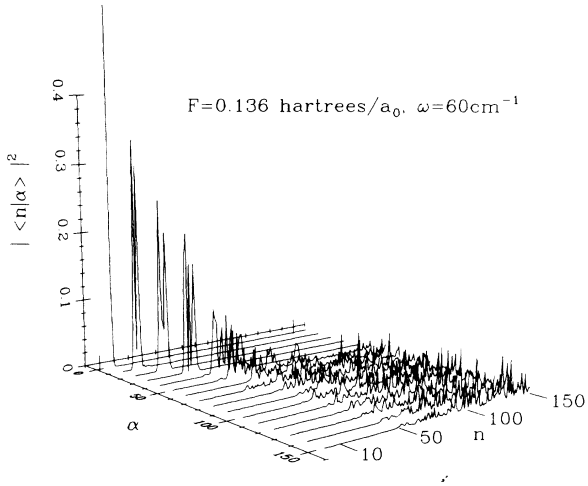


FIG. 3. The quasienergy eigenstates for a "moderate" intensity field. Note the sharp transition from narrow to broad eigenstates.

It is possible to make quantitative the idea of broad versus narrow quasienergy states by defining the width function[38]

$$W(\alpha)=\exp\left[-\sum_n |\langle n|\alpha\rangle|^2 \ln(|\langle n|\alpha\rangle|^2)\right] . \quad (11)$$

When the field is turned off, the width function is unity; whereas if the Floquet state $|\alpha\rangle$ is distributed evenly over $k$ Morse eigenstates, then $W(\alpha)=k$. Figure 4 presents an idealized version of the transition between these two extremes of narrow and broad Floquet states.

For a given field intensity and frequency, $W(\alpha)$ is a measure of now many Morse states overlap with a particular Floquet state. When $W(\alpha)$ is large the state $|\alpha\rangle$ provides the means for extensive excitation of the oscillator by the radiation. Figure 5 illustrates how the width varies with quasienergy state $|\alpha\rangle$ for four field strengths ($\alpha_W$ marks the onset of broad states). Note that while it is possible to rank Morse states according to their energy eigenvalues, the same cannot be done for the Floquet

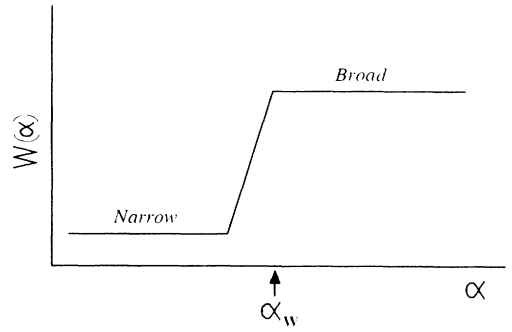


FIG. 4. Simplified illustration of the transition from narrow to broad states in the width function $W(\alpha)$.

states, because the quasienergies are only defined modulo $2\pi/\tau$. Therefore in Fig. 5 they are ranked according to their average energy, as defined by $\bar{n}\omega = \omega \sum_n n |\langle \alpha | n \rangle|^2$.

Ranked by average energy, the widths in Fig. 5 bear a strong resemblance to the idealized version presented in Fig. 4. Alternative ordering schemes are certainly possible; for example, one could simply rank the Floquet states by their width. Another approach is to abandon altogether trying to rank the quasienergy state and examine the widths of the Morse eigenstates when expanded in the quasienergy basis. The width function $W(n)$ is identical to Eq. (11), except that the sum is taken over $\alpha$ instead of $n$. The widths of the Morse states, shown in Fig. 6, are very similar to their $\alpha$ counterparts in Fig. 5 and confirm the distinction between narrow and broad states.

Both Figs. 5 and 6 indicate that the transition from narrow to broad states moves to lower energy (i.e., lower $n$ or $\alpha$) as the field intensity increases. This is a consequence of increasing importance of the dipole moment operator in establishing the character of the quasienergy states as $F$ becomes larger. Also apparent is a concomitant increase in the breath of the broad states. This increase follows an approximately $\overline{W} \sim \sqrt{F}$ dependence on field intensity, where $\overline{W}$ is the average width of the broad states.

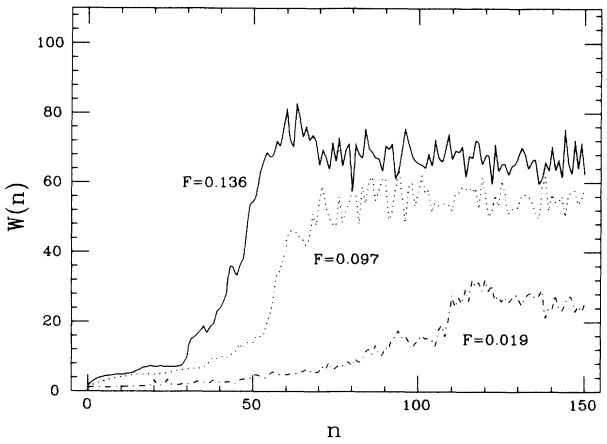


FIG. 6. Widths of the Morse eigenstates with respect to the quasienergy basis for a variety of field intensities. The frequency is $\omega = 60\ \text{cm}^{-1}$.

The variations in the width of the quasienergy states and the onset of broad states $\alpha_w$ as a function of field frequency are more complex. For example, as Fig. 7 shows, they are not monotonic in $\omega$. The onset of broad states shifts to small $\alpha$ (equivalently $n$) as $\omega$ increases, reaching a maximum in the vicinity of $\omega \simeq 170\ \text{cm}^{-1}$, but then shifts back to larger $\alpha$ as the frequency is increased further. The likely reason is that $\omega \simeq 170\ \text{cm}^{-1}$ in an average sense best satisfies resonance for this anharmonic system. Increasing $\omega$ implies that the radiation will lie above resonance for too many Morse levels; thus, excitation of the oscillator becomes less efficient. Similarly, decreasing $\omega$ implies that the radiation will be below resonance for too many levels, again lowering the excitation efficiency.

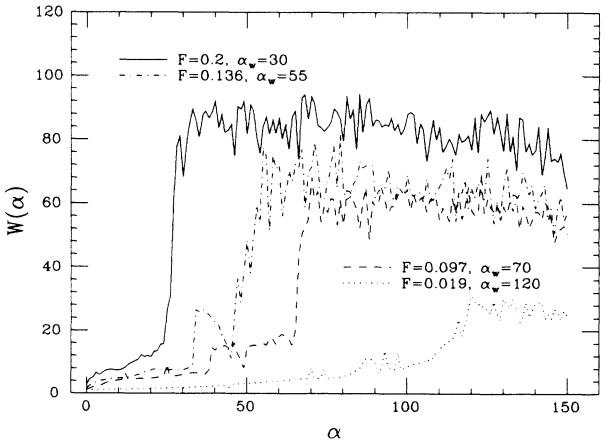


FIG. 5. Widths of the quasienergy states as a function of $\alpha$ for various field intensities. $\alpha_W$ indicates the approximate onset of broad states. The frequency is $\omega = 60\ \text{cm}^{-1}$.

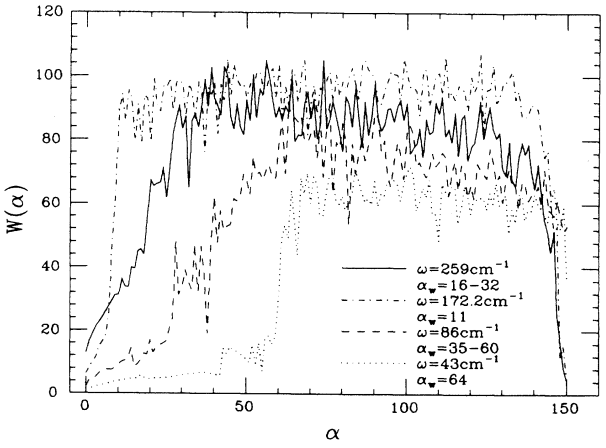


FIG. 7. Widths of the quasienergy states as a function of $\alpha$ for various field frequencies. $\alpha_W$ indicates the approximate onset of broad states. The field intensity is $F = 0.136$ hartree$/a_0$.

## IV. COMPARISON OF FLOQUET RESULTS TO SIMULATION

The quantum simulation of Morse oscillator dissociation by intense electromagnetic radiation reveals number of interesting dynamical features.[45] There is a sharp threshold for dissociation as a function of the intensity of radiation. Above threshold intensity the probability for dissociation at first increases rapidly as a function of time, as shown in Fig. 8 for a variety of initial states, but then the dissociation rate slows down considerably. For the undissociated portion of the oscillator, the probability of finding it be be in a particular eigenstate of the Morse oscillator varies in time, but remains localized within a relatively narrow band of Morse states. Similar behavior is found for a variety of frequencies ranging from well below resonance to above resonance; however, the threshold intensity required to achieve dissociation and the extent of dissociation vary as a function of frequency. In particular, the probability of dissociation[45] exhibits "resonances" that mimic those found in the microwave ionization of hydrogen and are attributed to the existence of stable periodic orbits.[30–32]

In this section we make use of the quasienergy states to understand the dissociation dynamics of the Morse oscillator observed by the quantum simulation of Ref. 45. Equation (5) indicates that excitation to high-lying oscillator states, or dissociation, is not possible if the initial state $n_0$ overlaps *only* with *narrow* Floquet states. Thus, the route to dissociation is via the *broad* states. Blümel and Silansky[37,38] base their analysis of the microwave ionization of hydrogen on a similar argument; only they assume that the broad states connect the initial state to "window" states which then ionize. Since the width function gives an idea of the number of Floquet states with which a particular Morse state overlaps, we expect $W(n)$ to resemble a plot of dissociation probability versus $n$. Such a comparison is presented in Fig. 9. The dissociation probability is taken at 18 field cycles, after which $P_{\rm dis}(t)$ changes little with time. Although there is rough agreement between the width function and $P_{\rm dis}(n)$, the correlation is not entirely satisfactory. The width function predicts dissociation to occur from initial Morse eigenstates significantly lower than observed from the simulation. The cause of this is that $W(n)$ does not distinguish between the broad and narrow states; rather, it indicates only an average width.

Let us instead define projection operators

$$\mathcal{P}_N = \sum_{\text{narrow}} |\alpha\rangle\langle\alpha| \tag{12}$$

and

$$\mathcal{P}_B = \sum_{\text{broad}} |\alpha\rangle\langle\alpha| \tag{13}$$

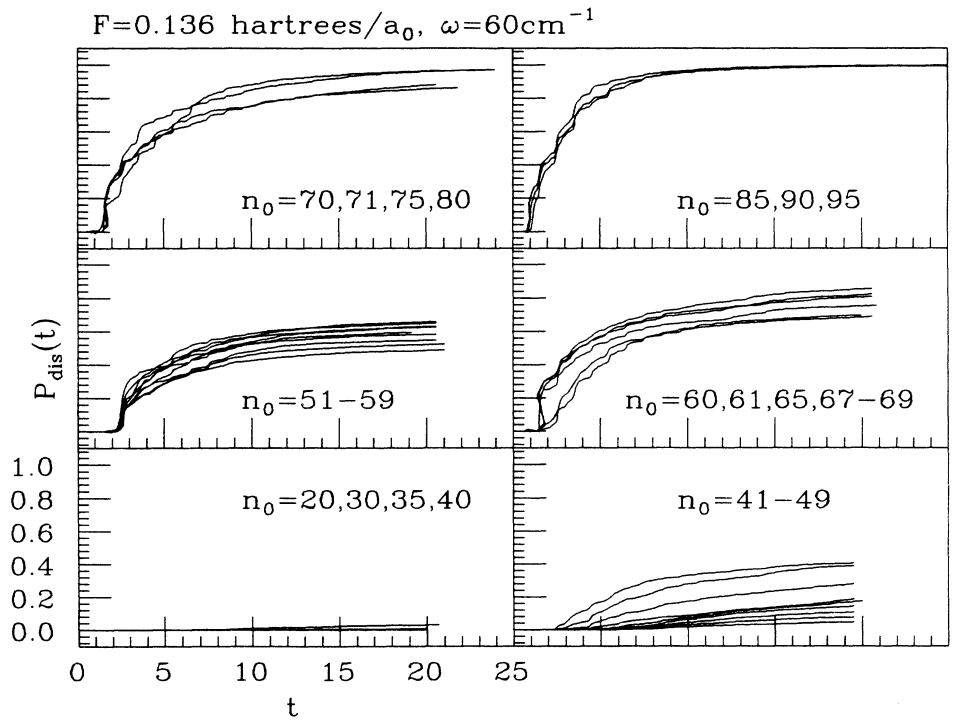


FIG. 8. Dissociation probabilities as a function of time for a wide range of initial Morse oscillator excitation as obtained from the quantum simulation.

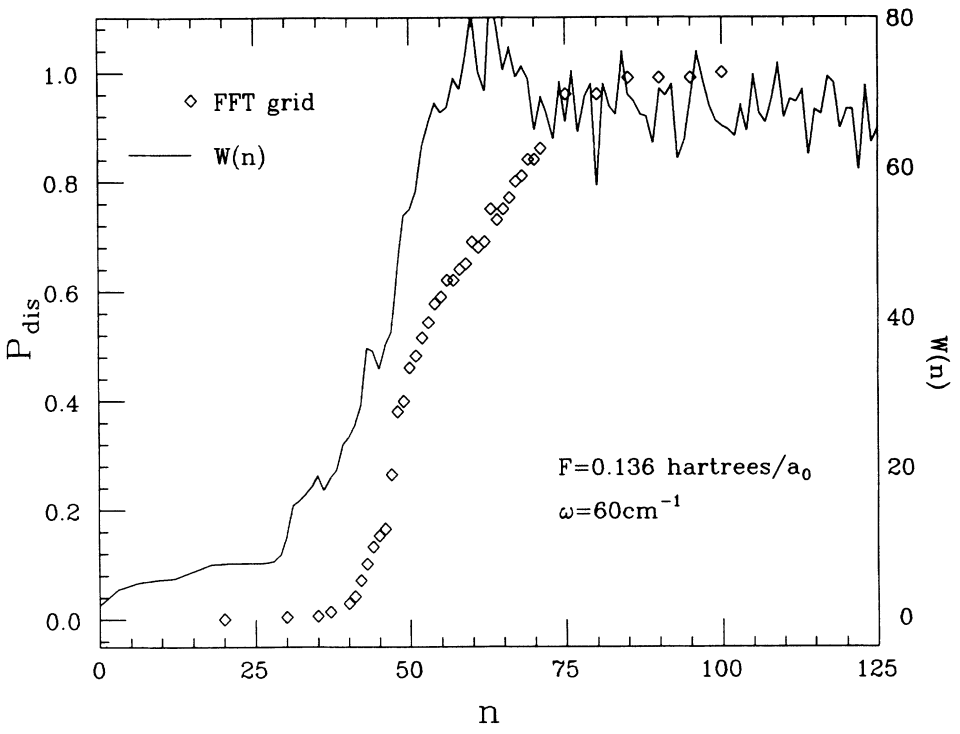


FIG. 9. Comparison of the width function $W(n)$ to the simulated dissociation probability as a function of initial Morse oscillator excitation.

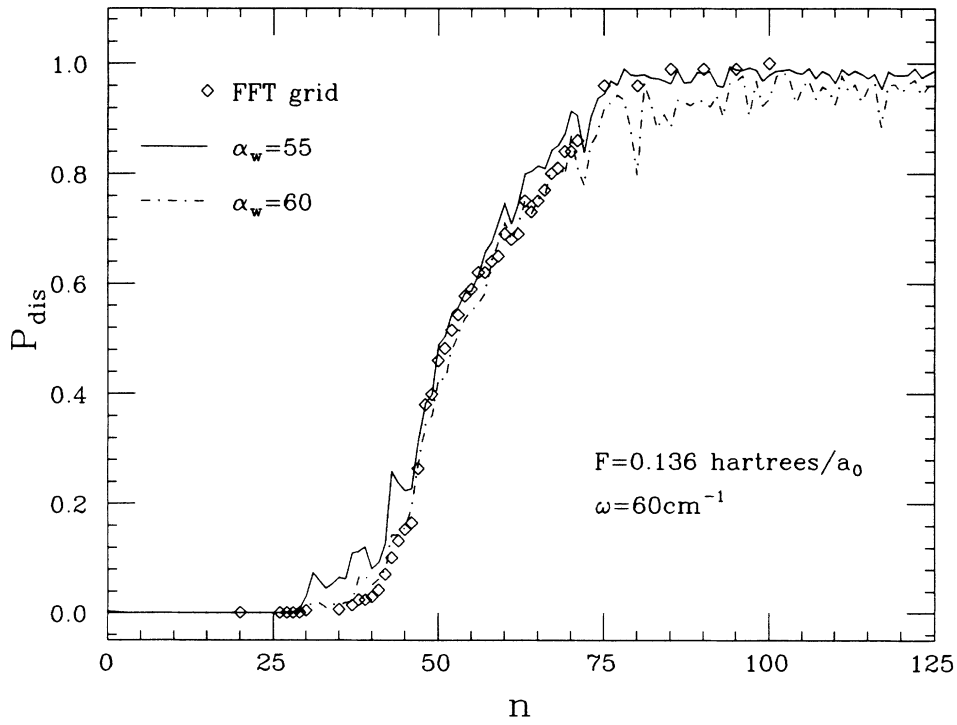


FIG. 10. Comparison of $P_B(n_0)$, the projection of the initial oscillator state onto the broad state subspace, and the dissociation probability predicted via the FFT grid method as a function of initial oscillator state. $P_B(n_0)$ is shown by the solid and dashed curves for two choices for the onset of broad states.

onto the narrow and broad quasienergy states, respectively. The assumption, based on Eq. (5), is that only the projection of the initial Morse state onto the broad state space is capable of contributing to dissociation. Therefore, we define a "dissociation probability"

$$P_B(n_0)=\langle \mathcal{P}_B n_0|\mathcal{P}_B n_0\rangle=\sum_{\text{broad}}|\langle n_0|\alpha\rangle|^2\,, \tag{14}$$

based on the probability that the initial oscillator state belongs to the broad state subspace. As Fig. 10 illustrates, there is good agreement between the projection of $n_0$ onto the broad states and they probability given by the simulation [calculated after 18 field cycles via Eq. (10)]. In reality, of course, the time-dependent exponential terms in Eq. (5) also play an important role. The results in Fig. 10, however, suggest that while they may influence the time dependence of the dissociation, the probability of whether or not the oscillator eventually dissociates is primarily determined by the projection of the initial state onto the broad states and is not dependent on time.

The assumption of the previous paragraph explains another observation from the simulation, namely, that after $P_{\text{dis}}(t)$ levels off in time, the bound portion of the wave function exhibits recurrences to states in the vicinity of $n_0$. Heller[57] has shown that these recurrences lead to a slowdown in the rate of phase space flow, and therefore to the decrease in dissociation rate observed in Fig. 8. Within the Floquet picture, we associate the slowdown in phase space flow with the complementary projection of $n_0$ onto the narrow quasienergy state space. This projection leads to localization of the oscillator, with *localization length* defined, for example, as

$$l(n_0)=\exp\left[-\sum_{\substack{\text{narrow}\\ \alpha}}|\langle n_0|\alpha\rangle|^2\ln(|\langle n_0|\alpha\rangle|^2)\Big/\sum_{\substack{\text{narrow}\\ \alpha}}|\langle n_0|\alpha\rangle|^2\right]. \tag{15}$$

Thus, if we assume that all the broad states lead to dissociation, then the remaining bound portion of oscillator remains localized to a relatively small range of Morse states. Casati and co-workers[34–36] have observed similar bound-state localization in their studies of H atom ionization. Localization in momentum space is also found for the periodically kicked rotor.[17–19]

The correlation between the probability that $n_0$ pro-

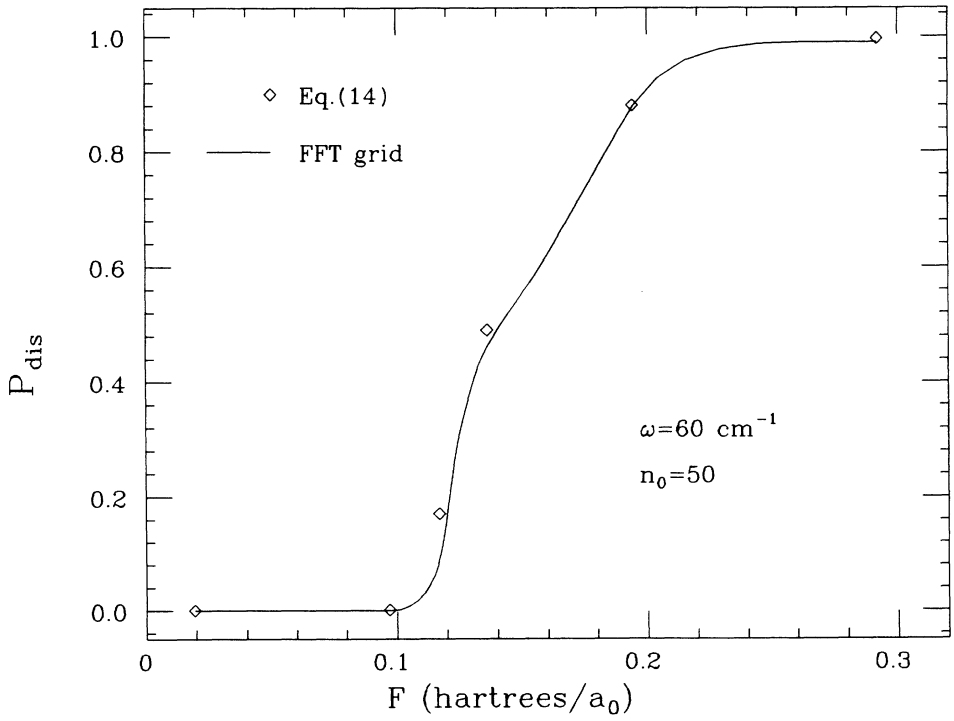


FIG. 11. Comparison of $P_B$, the projection onto the broad state subspace of the initial oscillator state, and the dissociation probability predicted via the FFT grid method as a function of field intensity. The choice for the onset of broad states is indicated by $\alpha_w$ in Fig. 5.

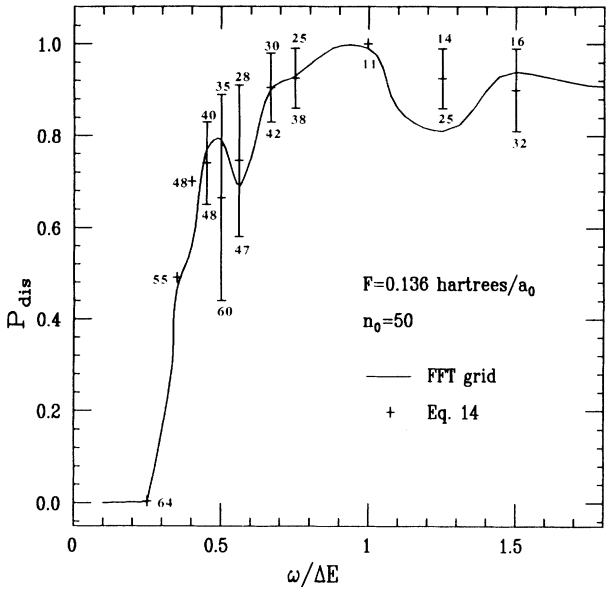


FIG. 12. Comparison of the projection of the initial oscillator state onto the broad state subspace and the dissociation probability predicted via the FFT grid method as a function of field frequency. The error bars indicate the variation in $P_B$ with the choice for the onset of broad states. The numbers next to the error bars represent the choice of $\alpha_W$.

jects onto the broad states $P_B$ and the simulated dissociation probability $P_{\text{dis}}$ with respect to their variation with the intensity and frequency of the radiation further supports the interpretation of the Floquet states made above. There is a threshold field intensity for $P_B$, shown in Fig. 11, that is in excellent agreement with the threshold for the actual dissociation probability. The variation of $P_B$ with $\omega$, in Fig. 12, also correlates well with dependence of $P_{\text{dis}}$ on laser frequency. The error bars for the points representing $P_B$ arise in the following way. As can be seen in Fig. 7, the distinction between broad and narrow Floquet states is sharper for some frequencies than others. Typically, the onset of broad states becomes difficult to ascertain when the dissociation probability is large and there is only a limited range of narrow states. The error bars in Fig. 12, represent the range of values of $P_B$ determined using various values of $\alpha_W$ from the region separating broad and narrow states in Fig. 7. Although this partially obscures the structure observed in the simulation, the overall agreement is good.

## V. CONCLUSION

The question of quantum chaos motivates much of the work on the microwave ionization of hydrogen atoms and the continuing study of the periodically kicked rotor. While stochastic diffusion of the electron in phase space summarizes the classical description of the microwave ionization problem,[30–32] localization and an absence of quantum chaos seem to be the accepted conclusion within the quantal description of that system.[34–36] A similar situation exists for the Morse oscillator. Wyatt and co-workers[39,46] have shown that a classical description of the dissociation of the HF molecule involves chaotic trajectories; however, a quantal wave packet under the same conditions is localized by cantori structures. Our work too shows the importance of localization in the quantum-mechanical description of the dissociation process. Within the Floquet analysis, however, this naturally follows from the structure of the quasienergy states.

The quasienergy states for a Morse oscillator in a strong laser field fall into two distinct classes: (i) Narrow states that resemble very much the Morse eigenstates themselves, and (ii) broad states that overlap with the entire range of Morse states having eigenvalues above a given threshold value. The resolution of the initial state of the Morse oscillator onto these two subspaces explains both the dissociation probabilities and localization observed by the quantum simulation of the oscillator dynamics. The underlying assumption is simple; broad states dissociate, whereas narrow states do not. By their nature, the narrow states imply localization of the oscillator. Within this picture the fate of the oscillator appears to be determined solely by its initial condition. More precisely, knowledge of the evolution of the system over one period is necessary to find the quasienergy states. Thus, the fact that the resolution of the initial oscillator state with respect to the quasienergy states determines its dynamics is a consequence of Floquet's theorem for periodically time-dependent linear differential equations.

Given the above interpretation of Morse oscillator dynamics, what is of interest is how the quasienergy states vary with the physical parameters of the system, for example the frequency and intensity of radiation and the initial state of the oscillator. Within the scope of the present study, the region of broad states, and the complementary region of narrow states are found to vary in a regular manner with all three of these parameters. Increasing the intensity of radiation increases the region of broad states. Because of the sharp transition from narrow to broad quasienergy states, this translates into a sharp threshold for dissociation. For the same reason, there is a sudden onset for dissociation with respect to the initial excitation of the oscillator. With respect to laser frequency, there is an optimum value that best satisfies resonance for the anharmonic Morse oscillator. Frequencies close to this value have a stronger influence on the oscillator than frequencies well removed from this value. Neither the size of the region of broad states nor the dissociation probability, however, have a monotonic dependence on the frequency of radiation. In fact the dependence is reminiscent of that found within the classical description of microwave ionization in hydrogen.[31] The agreement between the Floquet analysis and the quantum simulation supports the idea that the dissociation dynamics is largely a bound-state phenomenon.

*Present address: Department of Chemistry, University of Houston, 4800 Calhoun Road, Houston, Texas 77004.
†Present address: Department of Chemistry, E-3172 SRL Ford Motor Company, P. O. Box 2053, Dearborn, Michigan 48121.

[1]S. A. Rice and R. Kosloff, J. Phys. Chem. **86**, 2153 (1982).
[2]W. P. Reinhardt, J. Phys. Chem. **86**, 2158 (1982).
[3]B. J. Berne, N. De Leon, and R. O. Rosenberg, J. Phys. Chem. **86**, 2166 (1982).
[4]G. Wunner, U, Woelk, I. Zech, G. Zeller, T. Ertl, F. Geyer, W. Schweitzer, and H. Ruder, Phys. Rev. Lett. **57**, 3261 (1986).
[5]D. Wintgen and H. Marxer, Phys. Rev. Lett. **60**, 971 (1988).
[6]R. Blümel and U. Smilansky, Phys. Rev. Lett. **60**, 477 (1988).
[7]P. O'Connor, J. Gehlen, and E. J. Heller, Phys. Rev. Lett. **58**, 1296 (1987).
[8]E. J. Heller, Phys. Rev. A **35**, 1360 (1987).
[9]W. M. Visscher, Phys. Rev. A **36**, 5031 (1987).
[10]R. M. Stratt, N. C. Handy, and W. H. Miller, J. Chem. Phys. **71**, 3311 (1979).
[11]M. D. Feit, J. A. Fleck, Jr., J. Chem. Phys. **80**, 2578 (1984).
[12]G. Casati, B. V. Chirikov, F. M. Izraelev, and J. Ford, *Stochastic Behavior in Classical and Quantum Hamiltonian Systems,* Vol. 93 of *Lecture Notes in Physics,* edited by G. Casati and J. Ford (Springer-Verlag, Berlin, 1979), p. 334.
[13]D. L. Shepelyansky, Physica **8D**, 208 (1983).
[14]B. Dorizzi, B. Grammaticos, and Y. Pomeau, J. Stat. Phys. **37**, 93 (1984).
[15]J. Bellissard, *Stochastic Processes in Classical and Quantum Systems,* Vol. 262 of *Lecture Notes in Physics,* edited by T. M. Seligman and H. Nishioka (Springer-Verlag, Berlin, 1986), p. 24.
[16]H. Frahm and H. J. Mikeska, Phys. Rev. Lett. **60**, 3 (1988).
[17]S. Fishman, D. R. Grempel, and R. E. Prange, Phys. Rev. Lett. **49**, 509 (1982).
[18]D. R. Grempel, R. E. Prange, and S. Fishman, Phys. Rev. A **29**, 1639 (1984).
[19]E. Doron and S. Fishman, Phys. Rev. Lett. **60**, 867 (1988).
[20]T. Hogg and B. A. Huberman, Phys. Rev. Lett. **48**, 711 (1982).
[21]P. W. Anderson, Phys. Rev. **109**, 1492 (1958).
[22]P. W. Anderson, Rev. Mod. Phys. **50**, 191 (1978).
[23]K. A. H. van Leeuwen, G. v. Oppen, S. Renwick, J. B. Bowlin, P. W. Koch, R. V. Jensen, O. Rath, D. Richards, and J. G. Leopold, Phys. Rev. Lett. **55**, 2231 (1985).
[24]J. E. Bayfield, L. D. Gardner, and P. M. Koch, Phys. Rev. Lett. **39**, 76 (1977).
[25]J. E. Bayfield and P. M. Koch, Phys. Rev. Lett. **33**, 258 (1974).
[26]P. M. Koch, J. Phys. (Paris), Colloq. **43**, C2-187 (1982).
[27]P. M. Koch, K. A. H. van Leeuwen, O. Rath, D. Richards, and R. V. Jensen, Lect. Notes Phys. **278**, 106 (1987).
[28]E. J. Galvez, B. E. Sauer, L. Moorman, P. M. Koch, and D. Richards, Phys. Rev. Lett. **61**, 2011 (1988).
[29]J. E. Bayfield and D. W. Sokol, Phys. Rev. Lett. **61**, 2007 (1988).
[30]R. V. Jensen, Phys. Rev. A **30**, 386 (1984).
[31]J. G. Leopold and D. Richards, J. Phys. B **18**, 3369 (1985).
[32]D. A. Jones, J. G. Leopold, and I. C. Percival, J. Phys. B **13**, 31 (1980).
[33]V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer-Verlag, New York, 1978).
[34]G. Casati, B. V. Chirikov, and D. L. Shepelyansky, Phys. Rev. Lett. **53**, 2525 (1984).
[35]G. Casati, B. V. Chirikov, I. Guarneri, and D. L. Shepelyanski, Phys. Rev. Lett. **59**, 2927 (1987).
[36]G. Casati, B. V. Chirikov, D. L. Shepelyanski, and I. Guarneri, Phys. Rep. **154**, 77 (1987).
[37]R. Blümel and U. Smilansky, Phys. Rev. Lett. **58**, 2531 (1987).
[38]R. Blümel and U. Smilansky, Z. Phys. D **6**, 83 (1987).
[39]M. J. Davis and R. E. Wyatt, Chem. Phys. Lett. **86**, 235 (1982).
[40]R. B. Walker and R. K. Preston, J. Chem. Phys. **67**, 2017 (1977).
[41]M. E. Goggin and P. W. Milonni, Phys. Rev. A **37**, 796 (1988).
[42]B. V. Chirikov, Phys. Rep. **52**, 263 (1979).
[43]R. Heather and H. Metiu, J. Chem. Phys. **86**, 5009 (1987).
[44]R. Heather and H. Metiu, J. Chem. Phys. **88**, 5496 (1988).
[45]J. J. Tanner and M. M. Maricq, Chem. Phys. Lett. **149**, 503 (1988).
[46]R. C. Brown and R. E. Wyatt, Phys. Rev. Lett. **57**, 1 (1986).
[47]M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982).
[48]M. D. Feit and J. A. Fleck, Jr., J. Chem. Phys. **80**, 2578 (1984).
[49]H. F. Trotter, Proc. Am. Math. Soc. **10**, 545 (1959).
[50]K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[51]V. I. Arnold, *Ordinary Differential Equations* (MIT, Cambridge, MA, 1978).
[52]R. M. Wilcox, J. Math. Phys. **8**, 962 (1967).
[53]U. Haeberlen and J. S. Waugh, Phys. Rev. **175**, 453 (1968).
[54]M. M. Maricq, Phys. Rev. B **25**, 662 (1982).
[55]B. Jackson and H. Metiu, J. Chem. Phys. **86**, 1026 (1987).
[56]W. N. Sams and D. J. Kouri, J. Chem. Phys. **51**, 4809 (1969).
[57]E. J. Heller, Phys. Rev. A **35**, 1360 (1987).