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Three-dimensional molecular wave packets: Calculation of revival times from periodic orbits

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Abstract

We present a theoretical analysis of revivals and fractional revivals of three-dimensional wave packets, which describe the coupled vibrational motion of phosphacetyne (HCP) in its ground electronic state. The wave packets studied are chosen to evolve along the periodic orbits, which quantize the states in the three fundamental progressions. The revival times T_{rev} are found to depend strongly on the particular mode excited and on the mean excitation energy. Based on a semiclassical analysis, T_{rev} is shown to be determined by the dependence of the period of the orbits on the classical action along them. © 1998 Elsevier Science B.V.

The ability of quantum mechanical wave packets to regain their original shape after a considerable period of apparently irreversible delocalization has stimulated active research (see, for example, Refs. [1,2]). These phenomena, termed *revivals*, are the universal features of the temporal evolution of quantum mechanical systems [3]. They have been observed for electronic wave packets in Rydberg atoms [4,5], two-level atoms in cavities [6], and for molecular wave packets in diatomic molecules [7]. Partial localizations of the probability density at times shorter than the full revival time, known as *fractional revivals* [1,3,8,9], have also been observed [10,11]. They correspond to splitting of the initial wave packet into a set of separately moving sub-packets. Up to now, theoretical and experimental studies of revivals were mainly focused on systems whose eigenenergies depend on only one quantum number. In this Letter we present results for

a system whose energy depends on *three* vibrational quantum numbers – HCP in its electronic ground state, a molecule with a three-dimensional nonseparable potential and appreciable mixing of the vibrational degrees of freedom.

A time-dependent wave packet is a superposition of all stationary states $\psi_n(\mathbf{r})$ with energies E_n , i.e.

$$\Phi(\mathbf{r}, t) = \sum_n c_n \psi_n(\mathbf{r}) \exp(-iE_n t/\hbar), \quad (1)$$

where \mathbf{r} represents a point in the configuration space. If the eigenvalues E_n depend only on one quantum number n , we shall call such systems *one-dimensional* (1D), although the Hamiltonian can be a function of more than one spatial coordinate (like in the Kepler problem). In the 1D case, the analysis of the phase differences $\exp[-i(E_n - E_m)t/\hbar]$ between the eigenstates [1–3,8,9] reveals that the initial wave packet

becomes reconstructed with its original phases at the revival time

$$T_{\text{rev}} = 2\pi\hbar \left(\frac{1}{2} \frac{\partial^2 E}{\partial n^2} \right)^{-1}_{\bar{n}}, \quad (2)$$

where \bar{n} is the quantum number of the state that has the maximum probability in the wave packet expansion, Eq. (1). At this time, the autocorrelation function (which serves as an example of an experimental time-dependent signal),

$$|S(t)|^2 = |\langle \Phi(0) | \Phi(t) \rangle|^2, \quad (3)$$

recovers its initial amplitude and its original oscillation frequency. Fractional revivals [8], are observed at times mT_{rev}/k , where m and k are relatively prime integers ($m < k$). One can detect them in the autocorrelation function through an increase of the frequency of the time signal [11].

After the many investigations of 1D systems, one is beginning to study revivals in systems with spectra depending on more than one quantum number [12–14]. In particular, the revivals of two-dimensional Rydberg wave packets in a static electric field were studied in Refs. [12,13]. Recently, we presented the first evidence of the existence of revivals in a triatomic molecule (HNO) with significant coupling between the three vibrational degrees of freedom [14]. The similarities and differences between the revival patterns of the one- and the three-dimensional wave packets have been investigated in this earlier study. The two main findings, which motivated the current analysis, are the following: First, all attempts to calculate the revival time T_{rev} , the main observable, by straightforward application of the 1D expression Eq. (2) failed to provide something more than just qualitative estimates (see also the discussion below). A more sophisticated theory is required. Second, in more than one dimension the general structure of the autocorrelation function and the revival time in particular depend on the initial position of the wave packet in the configuration space. Unlike the 1D case, one can search, for example, for the optimal initial conditions for a clearest reconstruction of the wave packet at the revival times.

The new facets of multi-dimensional wave packet evolution call for an extension of the currently available theory, which explicitly takes into account the multi-mode character of the system. In this Letter we

demonstrate that a semiclassical theory based on periodic orbits [15] can be effectively used for this purpose. To this end, we investigate revivals for the triatomic molecule HCP in its electronic ground state. The central points are the variation of T_{rev} for the various modes with the mean energy of the wave packet and its semiclassical approximation in terms of periodic orbits.

The spectroscopy of the linear molecule HCP has been investigated in recent years, both experimentally [16,17] and theoretically [18,19]. The main focus of these studies is the isomerization from HCP to CPH and how this is encoded in the vibrational energy spectrum. Using an ab initio potential energy surface (PES) – various two-dimensional (2D) cuts through the PES are depicted in Fig. 1 – we have calculated the first thousand vibrational levels in an attempt to provide a consistent assignment. The variational calculations are performed for total angular momentum $J = 0$ and use the Jacobi coordinates R , the distance from H to the center-of-mass of CP, r , the CP separation, and γ , the angle between the vectors \mathbf{R} and \mathbf{r} (with $\gamma = 0$ for linear HCP). In what follows the energies are quoted with respect to the ground vibrational state (0,0,0). Most of the vibrational levels are assigned by visual inspection of the nodal structure of their eigenfunctions; representative plots can be found in Refs. [18,19].

The main observations, as far as they are relevant for the present investigation, can be briefly summarized in the following way.

(i) The spectrum has a high degree of regularity; this means that most of the levels up to an energy of about 2.0 eV are uniquely assignable in terms of three quantum numbers (v_1, v_2, v_3) .

(ii) Mode 1 is mainly associated with the R coordinate (H–CP stretching); the wave functions for the states $(v_1, 0, 0)$ are parallel to the R axis.

(iii) The fundamental frequencies of modes 2 and 3 ($\nu_2 = 1283 \text{ cm}^{-1}$ and $\nu_3 = 1234 \text{ cm}^{-1}$) are comparable in magnitude, which leads to a pronounced anharmonic (Fermi) resonance; as a consequence, the energy levels are grouped in distinctly defined blocks, so-called polyads with polyad quantum number $P = v_2 + v_3$.

(iv) The result of this strong mode mixing is that the wave functions for the overtone states $(0, v_2, 0)$ and $(0, 0, v_3)$ are rotated into the (r, γ) plane.

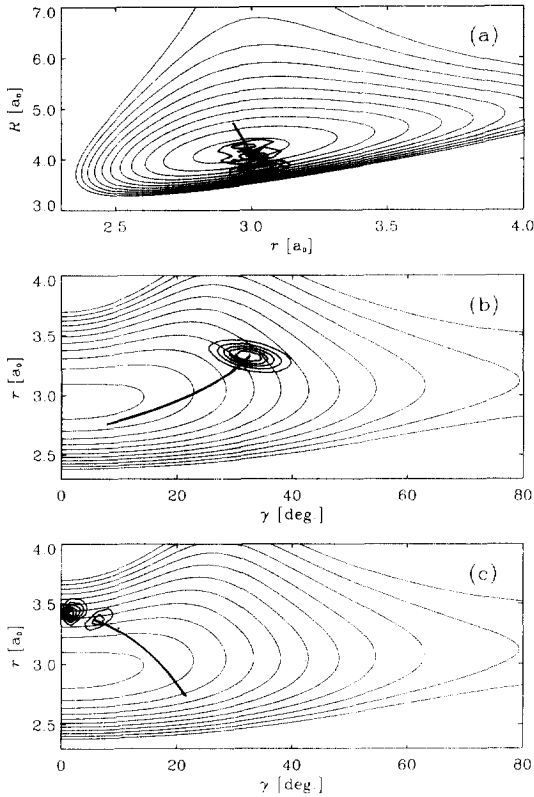


Fig. 1. Two-dimensional cuts through the HCP potential energy surface; the Jacobi coordinates R , r , γ are explained in the text. Also shown are the initial wave packets for the progressions (a) $(v_1, 0, 0)$, (b) $(0, v_2, 0)$, and (c) $(0, 0, v_3)$; the corresponding maximum probability quantum numbers \bar{v}_k are 5, 7, 7, respectively. The thick solid curves indicate the trajectories of the center of mass of the wave packets after three classical periods of oscillations. These trajectories are almost indistinguishable from the POs with energies equal to the mean energies of the wave packets.

(v) It is found that stable periodic orbits (POs) accurately describe many of the quantum mechanical results. In particular, the bifurcational analysis [19] showed that the classical phase space is regular in the same energy range, in which the quantum states are assignable. Besides, the nodal lines of the wave functions belonging to the pure progressions $(v_1, 0, 0)$ etc. are perfectly aligned along the corresponding POs.

The latter point is crucial for the present investigation, for we can construct particular wave packets, which move always along the underlying POs. This enables us to use the WKB theory even for the long-time quantum dynamics and to predict accurately the revival times.

Each wave packet considered is prepared by using the states in one of the three pure progressions $(v_1, 0, 0)$, $(0, v_2, 0)$, or $(0, 0, v_3)$. The coefficients c_{v_k} in Eq. (1) are taken to be Gaussian distributions [1] centered around some mean quantum numbers \bar{v}_k . By changing \bar{v}_k one can study the dependence of the revival times on energy. The standard deviation of the Gaussians is chosen to be $\sqrt{3}$. The initial wave packets constructed in this way are not necessarily bell-shaped functions in the coordinate space (see Fig. 1); nevertheless, they are still well localized. Wave packets are propagated for 14 ps, a period covering several revivals in all modes. Although pure progressions are excited, the packets encompass multi-dimensional motion as is clear from Fig. 1 showing the early-time trajectories of the centers of the wave packets.

The resulting autocorrelation functions, Eq. (3), are presented in Fig. 2. The *general* temporal evolution is similar in the three cases. The signal initially oscillates at the classical frequency [8] of the corresponding mode, while its amplitude gradually decreases as the wave packet dissolves. At later times, changes in the signal frequency become observable, indicating the appearance of fractional revivals. The fractional revivals up to the order $1/6$ are clearly recognizable in Fig. 2. A vibrogram representation [11,14] reveals revivals even up to the order $1/12$. The oscillatory patterns in these examples are so transparent because of the simplicity of the spectra used for constructing the initial wave packets (shown in the insets). As demonstrated below, $|S(t)|^2$ has a more complicated behavior, if additional states are incorporated. The original period and amplitude of $|S(t)|^2$ are recovered at $T_{\text{rev}}/2$, when the wave packet is fully reconstructed [8]. At later times the temporal evolution more or less repeats itself.

It is clear from Fig. 2, that the revival times in all three progressions are drastically different. Mode 1 has the shortest revival time, $T_{\text{rev}}^{(1)} \approx 0.5$ ps; this suggests that this mode has the largest anharmonicity. The other two revival times, $T_{\text{rev}}^{(2)}$ and $T_{\text{rev}}^{(3)}$, are an order of magnitude larger, being 4.8 ps and 7.2 ps, respectively. The revival times depend in different ways on the mean energy of the wave packet, as is shown in Fig. 3. While $T_{\text{rev}}^{(1)}$ is almost constant and while $T_{\text{rev}}^{(3)}$ depends only weakly on energy, the revival time for mode 2 exhibits a pronounced nonmonotonic energy dependence.

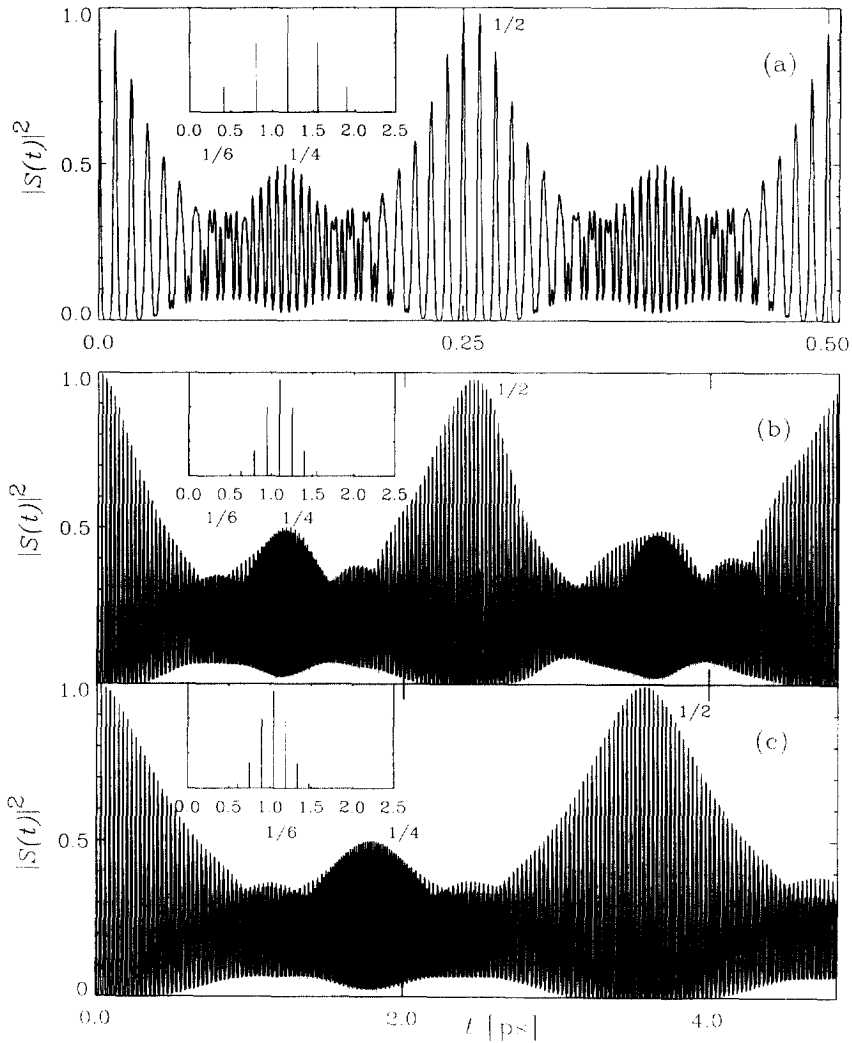


Fig. 2. Autocorrelation functions $|S(t)|^2$ for the wave packets shown in Fig. 1. The numbers 1/6 etc. indicate the fractional revival times. Note the difference in the time scales in the first panel and the second and the third lower panel. The insets show the respective distributions of normalized amplitudes $|c_{v_k}|^2$ versus energy (in eV) of the states $(v_1, 0, 0)$ etc.

At first glance, it should be possible to estimate the revival times of these especially constructed wave packets with the 1D theory. In order to do so, one fits the energies for a particular progression, weighted by the probabilities $|c_{v_k}|^2$ with which they contribute to the wave packet, to the Dunham expression of the form

$$E(v_1, v_2, v_3) = \sum_{k=1}^3 \nu_k (v_k + 1/2)$$

$$+ \sum_{k=1}^3 \sum_{l \geq k}^3 \alpha_{kl} (v_k + 1/2)(v_l + 1/2) + \dots \quad (4)$$

The Dunham expansion is, in essence, a Taylor expansion of the energy in terms of quantum numbers. After that, the diagonal first-order anharmonicity α_{kk} is used in Eq. (2). Excellent agreement with the results from the full-dimensional calculation is found for mode 1, the least coupled mode in the system [19]. However, for the other two modes, which are involved in the

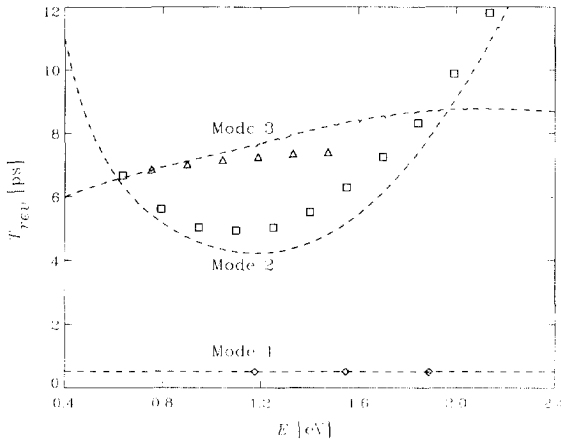


Fig. 3. The dependence of the full revival times on the mean excitation energy in modes 1–3. The dashed lines show the semiclassical estimations according to Eq. (7).

Fermi resonance, the fit turned out to be highly unstable with respect to the order of the Dunham expansion. Inclusion of anharmonicities proportional to v_k^3 or v_k^4 changes the revival time as estimated by the 1D expression in an unpredictable manner! Let us consider the wave packet for mode 2 with a mean energy of 0.63 eV as an example. If only the terms up to v_2^2 are included in the Dunham series, the 1D revival time is 9.3 ps; adding the v_2^3 term changes the coefficient in Eq. (2) such that the revival time becomes 23.4 ps. Finally, with the v_2^4 term included, one gets 8.9 ps. The real revival time, however, is 6.7 ps. The main problem is that the perturbation theory expansion, on which the Dunham fit is based, can be highly inadequate for describing strongly coupled systems – *even if pure progressions are considered*. This has long been recognized in molecular spectroscopy. For this reason non-perturbative extensions of the Dunham expansion are introduced in the form of so-called effective Hamiltonians in order to fit observed spectra [20].

A more rigorous approach, that does not suffer from these shortcomings, is based on semiclassical theory. Introducing the classical actions I_k ,

$$I_k = \frac{1}{2\pi} \oint_{C_k} \mathbf{p} \cdot d\mathbf{q} = v_k + 1/2, \quad (5)$$

related to the quantum numbers v_k through the EBK quantization conditions (C_k are the topologically distinct contours on the 3D torus) [15], one can write

$$\frac{1}{\hbar} \left(\frac{\partial^2 E(v_1, v_2, v_3)}{\partial v_k^2} \right)_{\bar{v}_k} \approx \left(\frac{\partial^2 H(I_1, I_2, I_3)}{\partial I_k^2} \right)_{E_{I_k}}, \quad (6)$$

where $H(I_1, I_2, I_3)$ is the classical Hamiltonian, expressed in action-angle variables. These variables are known to exist (locally) provided the motion is regular, which indeed is the case for the energy regime considered here [19]. Note, that the function on the right-hand side of Eq. (6) is now continuous. There exist a number of numerical methods for performing the transformation to action-angle variables (see, for example, Ref. [21]). However, they are difficult to apply here, mainly because two of the three actions must be kept constant in Eq. (6) when calculating the finite differences.

The existence of stable POs provides a simple means for calculating the derivatives in Eq. (6) in a numerically convenient way. As mentioned before and demonstrated in detail in the previous two publications on HCP, the stationary wave functions for states $(v_1, 0, 0)$, $(0, v_2, 0)$, and $(0, 0, v_3)$ and therefore our time-dependent wave packets follow closely the POs (see Fig. 1). These POs belong to the three fundamental families of trajectories, that emanate from the minimum of the potential and form three stable branches of the bifurcation diagram [19]. It is checked, that the orbits in each family quantize the states in one of the progressions considered above, if the zero-point energy in the remaining two transverse coordinates is taken into account [22]. Therefore the orbits for the k th mode may serve as topologically independent contours used in the definition of the action variable I_k . At a particular energy E , I_k is just the classical action along the corresponding periodic orbit at this energy, while $\partial H / \partial I_k$ is the angular frequency along this orbit. Thus, Eq. (2) can be written as

$$T_{\text{rev}}^{(k)}(E) = 4\pi \left(\frac{\partial \omega_k}{\partial I_k} \right)_E^{-1}, \quad (7)$$

where $\omega_k = 2\pi/T_k$ and T_k is the period of the corresponding orbit. Continuity of the frequencies ω_k is guaranteed by the continuity of the different branches of the bifurcation diagram [19]. Eq. (7) is exact for the 1D Morse oscillator.

The revival times calculated from this semiclassical relation are compared in Fig. 3 with the results

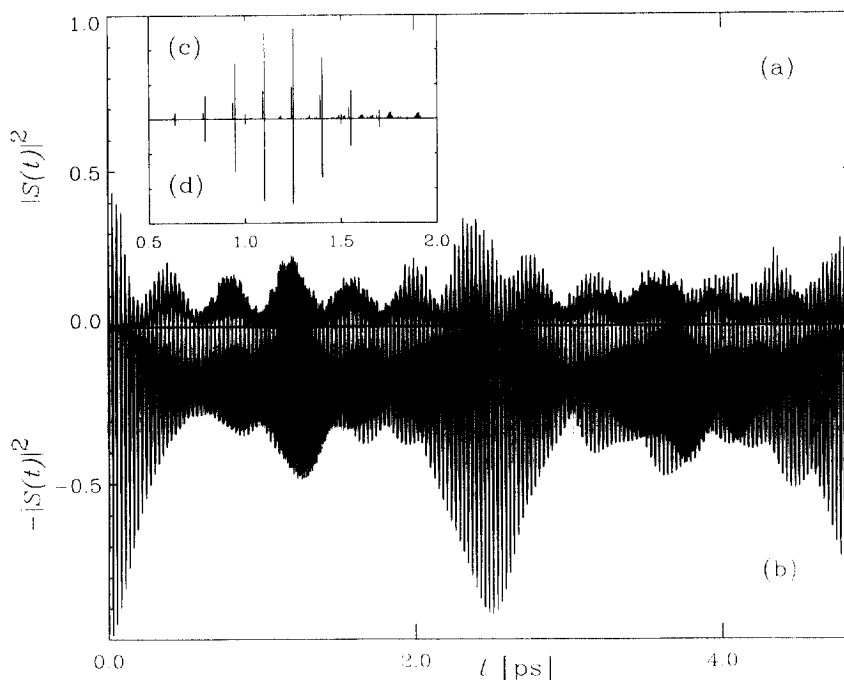


Fig. 4. (a) Autocorrelation function $|S(t)|^2$ for the Gaussian wave packet started close to the PO for mode 2; the mean energy is 1.2 eV. (b) The corresponding autocorrelation function for the packet built on the pure progression $(0, \nu_2, 0)$ with the same mean energy as in (a). The insets (c) and (d) show the corresponding distributions of normalized amplitudes $|c_k|^2$ versus energy (in eV) of the states included in the wave packets.

from the purely quantum mechanical calculations and satisfactory agreement is observed. In particular, the nonmonotonic energy dependence for mode 2 is well reproduced. The wave functions for mode 2 have a clear-cut nodal structure up to very high energies and therefore it is also possible to follow $T_{\text{rev}}^{(2)}$ up to large values of E . In view of the Eq. (7), the dependence of the revival time $T_{\text{rev}}^{(2)}$ on energy is due to the changing anharmonicity $\partial\omega_2/\partial I_2$ of the potential along the periodic orbits. This effective potential has the smallest anharmonicity at low energies, which is natural, and at high excitation energies, which is certainly a surprise.

The significance of Eq. (7) and the PO approach in general goes beyond the accurate calculation of the revival time. In more than one dimension it is not a priori clear where to place the initial wave packet in order to obtain pronounced revivals. However, robust POs, like those used in this study, can guide us in choosing reasonable starting conditions. If we initially place a Gaussian-type wave packet on a particular PO, it is likely to stay in the vicinity of the orbit and there-

fore to show revival structures. This is demonstrated for mode 2 in Fig. 4a, where we show the autocorrelation function for a Gaussian wave packet that was started close to the corresponding orbit. The resulting spectrum $|\langle\Phi(0)|\psi_n\rangle|^2$ depicted in Fig. 4c contains – in addition to the pure states $(0, \nu_2, 0)$ – also combination bands such as $(0, \nu_2 - 1, 1)$, $(0, \nu_2 - 2, 2)$ etc. within a given polyad. As a consequence of the extra terms the general appearance of the signal changes significantly; more structures come to existence and the revivals are less complete. However, the revival time remains basically unchanged and the degree of wave packet reconstruction is still fairly high. For comparison the results obtained with the pure states $(0, \nu_2, 0)$ are shown in Figs. 4b,d.

In summary, we have demonstrated that the revival times of multi-dimensional wave packets evolving along periodic orbits can be accurately predicted in a semiclassical way using the frequency of the orbit as a function of the action along the orbit. The POs can also be used to find the initial conditions for wave

packets, that will show pronounced revivals. The natural question raises as to whether such wave packets can be prepared in experiment. We hope that the PO approach, valid both in the low- and the high-energy regimes and, in principle, insensitive to the question of assignability of the states from which the wave packet is constructed, sheds light on the long-time quantum dynamics of multi-dimensional systems. More details of revivals in multi-mode systems and their relation to periodic orbits will be given in a later, more complete publication.

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