

Molecular Wavepacket Decomposition by Nonlinear Interferometry

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We show that nonlinear interferometry with pairs of phase-locked pulse-pairs can determine the complex overlap of an evolving excited-state nuclear wavepacket with a collection of wavepackets moving in specified ways in the ground-state potential. We outline a procedure through which this information can be inverted to yield the form of an evolving wavepacket directly from experimental data.

It is a basic notion that the wave function of a system can be expressed as a superposition of any complete set of states with coefficients given by complex overlaps. Opportunities to measure a complete set of overlaps for an evolving nuclear wavepacket are rare, however. We showed earlier that interferometry experiments with a pair of electronically resonant phase-locked pulses provide the overlap between an evolving wave function in an excited state and the stationary vibrational state from which it originated.¹ To specify the nuclear state completely, one needs to know its overlaps with a full manifold of vibrational wave functions.

Here we investigate a scenario for nonlinear optical measurements with *pairs* of phase-locked pulse-pairs that was previously considered as a means of preparing and measuring superpositions of wave functions of differently handed states of a chiral molecule.² A related technique has been implemented as a photon-echo probe of solvation dynamics.^{3,4} We show that wavepacket interferometry with pairs of pulse-pairs yields the overlaps of an evolving polyatomic wave function with a set of experimentally determined wavepackets of specified displacements and momenta. Contributions competing with the relevant overlaps are typically small, can be averaged away with sequences of related measurements, or occur at distinguishable interpulse-pair delays. Under limiting conditions, one may obtain an exhaustive set of overlaps with multi-mode Glauber coherent states.

The Hamiltonian has a molecular part $H = |g\rangle H_g \langle g| + |e\rangle H_e \langle e|$ and interactions with four resonant pulses $V_j(t) = -\mu(|e\rangle \langle g| + |g\rangle \langle e|) A_j(t-t_j) \cos[\Omega(t-t_j) + \Phi_j(t-t_j)]$. The measured quantity is the interference contribution to the *e*-state population, which can be isolated experimentally.¹ Since the signal is proportional to $A_1 A_2 A_3 A_4$, we need only a perturbative expression through first order in each $\tilde{V}_j$, which can be obtained from

$$e^{-iH_e t_d} \langle e | \tilde{\Psi}(t > t_d) \rangle = \{U_A + U_B + U_C + U_D + T_A + T_B + T_C + T_D\} \times e^{iH_g(t_w+t_p)} |\Psi_g\rangle. \quad (1)$$

There are 1-pulse contributions such as $U_c = e^{-iH_e t_d} P_3 e^{-iH_g(t_w+t_p)}$ and 3-pulse terms such as $T_c = P_4 e^{-iH_g(t_d+t_w)} P_2^\dagger e^{-iH_e t_p} P_1$, where the P_j are *pulse propagators*.⁵ The wavepackets of particular interest are shown in Fig. 1. The terms in $\langle \tilde{\Psi} | e \rangle \langle e | \tilde{\Psi} \rangle$ proportional to all four field strengths are

$$S_{\text{int}}(t_d) = 2\text{Re} \langle \Psi_g | T_A^\dagger U_A + T_B^\dagger U_B + T_C^\dagger U_C + T_D^\dagger U_D | \Psi_g \rangle. \quad (2)$$

The A through D terms correspond to *overlaps* between the eight wavepackets in Eq. 1; cross-terms do not influence the signal. For arbitrary delays only the sum Eq. 2 is measured, but basic features of nuclear wave-function evolution in polyatomic molecule suggest circumstances where simultaneous contributions can be avoided.

The A- and B-terms can be eliminated by spectral selection (finite bandwidth) as a result of the Stokes shift during *e*-state evolution in a multimode system and by $t_w (= t_3 - t_2)$ averaging motivated by the multiply harmonic nature of *g*-state motion when the intrapulse-pair delays $t_p (= t_2 - t_1)$ and $t_d (= t_4 - t_3)$ are relatively short. In the C- and D-term interference signals, evolution during the waiting time, t_w , takes place in the *g*-state potential, and both terms repeat themselves when t_w is increased by a common multiple of the periods of the Raman active modes. Since t_p is short, the wavepacket created by the first pulse is still close to the Franck–Condon point when the second pulse dumps it to the ground state (see for example the right panel in Fig. 1). Subsequent motion near the potential minimum starts with small displacements and momenta in the Raman active modes. The single-mode phase-space diagrams

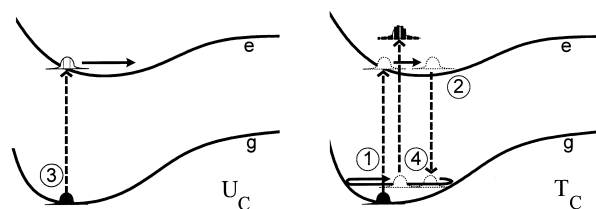


Fig. 1. Target wavepacket (left) for decomposition via overlap with reference wavepackets (right).

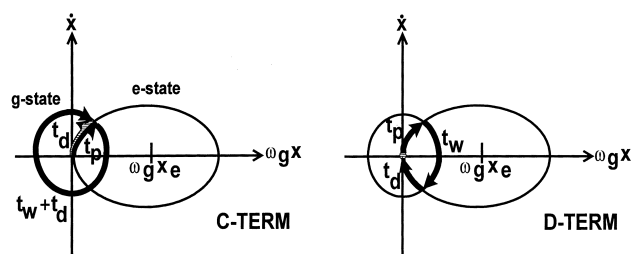


Fig. 2. Single-mode trajectories of target (hatched) and reference (solid) wavepackets overlapped in the C- and D-term signals.

(below) show that $t_p \approx t_d \approx \delta$ much shorter than the active-mode periods can produce nonvanishing C- and D-signals. These contribute at different waiting times: $t_w(\text{C}) + \delta t \approx \tau_g^{\text{FC}}$ must be a near common multiple of mode periods, while $t_w(\text{D}) \lesssim h_g^{\text{FC}}$ must be just less than a common odd multiple of the half-periods. Simple analysis outside the short-delay case is also possible for systems with one high-frequency mode and several lower-frequency vibrations. We are presently carrying out wave packet-dynamical studies in various hetero-substituted methane-halides.^{6,7}

When only the C-term contributes, the signal reduces to $S_{\text{int}}(t_d) = 2\text{Re}\langle\psi_g|T_C^\dagger U_C|\psi_g\rangle$. In the short-pulse limit the signal is proportional to $\text{Re}\{\langle\alpha|\xi(t_d)\rangle e^{i\phi_d}\}$, the overlap between the wavepacket $|\xi(t_d)\rangle = e^{-i(H_e - \Omega_d)t_d} e^{-iH_g(t_w + t_p)}|\psi_g\rangle$ and a reference state $|\alpha\rangle = e^{-iH_g(t_d + t_w)} P_2^\dagger e^{-iH_e t_p} P_1|\psi_g\rangle$. To the extent that various choices of t_p and t_w provide an exhaustive set of $|\alpha\rangle$'s, an experiment of this kind would determine the amplitudes necessary to specify the excited-state nuclear wave function at time t_d .

Even in the more general situation where this coherent-state picture does not apply, a well-defined inversion procedure can yield the target wavepacket $U_c|\Psi_g\rangle$ from its measured overlaps with a family of reference states $T_c|\Psi_g\rangle$. If we regard the sig-

nal for various t_p, t_w as elements of column vector, these data form the inhomogeneous part of an overdetermined system of algebraic equations whose solution is the target wavepacket. We are currently testing this approach on a photodissociative model system using singular-value decomposition plus back substitution.⁷

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