Computational Study of Many-Dimensional Quantum Energy Flow: From Action Diffusion to Localization

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Many-dimensional quantum calculations of energy flow are presented, revealing dynamical scaling in agreement with theoretical predictions. A model system of coupled anharmonic oscillators which undergoes a localization transition as a function of coupling strength was studied. For strong coupling, action diffusion is clearly seen. For near critical coupling, the average survival probability varies inversely with time but shows no simple relationship to the average extent of the spread of the wave function in action space.

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The problems of the origin of chaos and irreversibility in quantum mechanical systems are under intense investigation today. The analytical tools of semiclassical analysis and random matrix theory have led to many interesting conjectures about these problems which have been tested through detailed quantum mechanical calculations on systems having few dimensions [1]. These same problems have had a long fascination for chemical physicists in their quest to understand how energy flows in molecules. The extent and rate of energy flow in a molecule is important in determining the validity of statistical theories of reaction rates and for understanding the spectra of highly excited molecules [2]. The typical energy flow problem differs from the model problems previously studied in quantum chaos theory, primarily in being a problem of rather high dimensionality. High dimensionality provides both new phenomena and new limits for understanding chaos and irreversibility. New analytical tools are important for understanding the problem, and computational approaches typically have been difficult to apply. Building on recent computational progress, in this paper we present calculations on a many-dimensional quantum system which mimics many features of molecules. We find agreement with results of recent theories [3,4] which connect the problem of quantum localization and energy flow in high-dimensional systems with the problem of Anderson localization in disordered solids [5,6].

Energy flow in molecules predominantly occurs through a series of Fermi resonances between nonlinear oscillators. In classical systems the overlap of different Fermi resonant regions leads to chaotic dynamics and a global energy flow [7]. The universal classical mechanism for weak energy flow is Arnold diffusion which also arises in many-dimensional systems through numerous resonant overlaps. Quantum mechanical calculations also implicate Fermi resonances in global energy flow [8,9]. The Fermi resonance mechanism implies that energy transport is local in quantum number space: Only states which have nearly equal quantum numbers in the unperturbed representation are directly connected. This is the basis of the analogy to Anderson localization. Using an approximate mean field theory, Logan and Wolynes studied the energy transport in a quantum mechanical many-dimensional Fermi resonant system with random frequencies for the unperturbed oscillators [3]. Their theory suggests that in a high-dimensional quantum mechanical system there is a phase transition from having localized quantum states to delocalized quantum states in which energy can flow freely through the molecule. This transition occurs when the Fermi resonant coupling is comparable in magnitude to the inverse of the local density of states, the density of those states directly coupled to a given state. At the transition there is critical behavior of the rate of energy flow. Significant differences from the naive golden rule estimate of the energy flow rate are obtained at high values of the coupling strength. Using the general notion that the transport can be described using local random matrix models, Schofield and Wolynes later presented scaling arguments for energy flow, which suggest that in the strongly delocalized regime the dynamics is diffusive on the constant energy shell in quantized action space [4]. This perspective uses an analogy with the classical action diffusion earlier derived for resonantly interacting harmonic oscillators [10] and which has been shown to occur in low-dimensional chaotic systems [11]. The scaling arguments suggest also that near the transition, quantum coherences of different classical paths lead to rather slower energy transport, using reasoning modeled upon the scaling theory of Anderson localization [6]. Although these molecular analyses share the action diffusion picture with theories of quantum chaos in the kicked rotor [1,12], they differ significantly from those theories which use the Anderson localization concept in its one-dimensional incarnation,

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which lacks a sharp transition at nonvanishing coupling strength.

At the same time as these analytical developments, considerable progress has been made in the computational attack on the quantum energy flow problem. The development of the RRGM algorithm [13] and the Chebyshev time propagation [14] have made it possible to study energy flow in specific molecules such as 21 mode benzene [15]. It is now possible to study the quantum transport in the more abstract many-dimensional Fermi resonant model used in the analytical theories. Atkins and Logan have qualitatively interpreted numerical studies on a three oscillator system using the Anderson transition analogy [9]. In this paper we present quantitative computational evidence for the transition in higher-dimensional systems. We discuss the way in which energy transport varies with the coupling strength and focus on the scaling behavior of the average survival probability in the many-dimensional Fermi resonance system.

We consider quantum energy transport in a model anharmonic system involving $N = 6$ Morse oscillators coupled through cubic interaction terms. In mass-scaled, approximately normal coordinates the total Hamiltonian is

$$H = \sum_{\alpha}^{N}\left[\frac{1}{2}P_{\alpha}^{2} + D_{e}(1 - e^{-a_{\alpha}Q_{\alpha}})^{2}\right] + \frac{\phi}{3!}\sum_{\alpha,\beta,\gamma\in\mathrm{nn}}^{N} Q_{\alpha}Q_{\beta}Q_{\gamma}\,. \qquad (1)$$

The triple sum is over all nearest-neighbor combinations, with modes 1 and 6 coupled. The fixed dissociation energy for the Morse potentials is $D_e = 4$ eV and the a_α are chosen such that each harmonic frequency $\nu_\alpha = a_\alpha\sqrt{2D_e}/2\pi$ falls randomly in the interval [1000 cm $^{-1}$, 1004.4 cm $^{-1}$], giving an average of $\nu = 1002.2$ cm^{-1}. This model serves as a local random matrix example, representative generally of molecular systems with a homogeneous isotropic state space [16]. The basis functions used for the matrix representation of H are direct products of Morse oscillator functions, $|m_j\rangle = \prod_{\alpha=1}^{N}|v_{\alpha}^{(j)}\rangle$. The quantum number for each mode assumes the values 0,1,...,$v_{\max}$, so that the dimension of the direct product space is $d = (1 + v_{\max})^N$. At time $t = 0$, the initial wave packet $\Psi(0)$ was chosen as one of the 252 basis functions with five quanta, such as $|0\rangle|3\rangle|1\rangle|0\rangle|0\rangle|1\rangle$; for later averaging of dynamical quantities, the time dependence of each member of an ensemble was computed. Converting to the approximate algebraic coupling strength $\phi' = (\hbar/4\pi\nu)^{3/2}\phi$, application of the localization criterion of Ref. [3] gives an estimate of $\phi_c' = 1.2$ cm $^{-1}$ [17]. Calculations were carried out for nine values of ϕ'/ϕ_c' in the range 0.635–6350, selected at logarithmic intervals. Throughout the text and figures $\log = \log_{10}$.

Two time-dependent dynamical quantities were computed for individual initial states. These are the survival probability, $S(t)$, and the extent of the spread of the wave function in action space, $R(t)$. $S(t)$, the absolute square of the amplitude of finding the time evolving wave packet overlapping the initial wave packet, is accessible experimentally either directly or, using Fourier transform techniques, via the spectrum [18]. $S(t)$ was computed by evaluating the residues of the Green function at the exact eigenenergies. In the N-dimensional quantized action space, each axis represents the various quantum numbers for one of the Morse oscillators and each basis state for the N-oscillator system is represented by a lattice point. If n_0 denotes the initial lattice point at $t = 0$, then for $t > 0$ the extent of the spread of the wave packet in action space is measured by the dimensionless quantity $R(t) = \langle\Psi(t)|\,(n - n_0)^2|\Psi(t)\rangle^{1/2}$. In order to compute $R(t)$, we need the amplitudes $c_j = \langle m_j|\Psi(t)\rangle$, the projections of the time evolving wave packet upon the various multimode basis functions. In these studies, the maximum single mode quantum number is $v_{\max} = 6$, so that the dimension of the direct product space is $d = 117{,}649$. In order to reduce the size of this basis set, modes 1–3 were merged with an energy cutoff of 5921 cm $^{-1}$ and modes 4–6 were merged with the same energy cutoff, resulting in a contracted basis of 3136 states.

$S(t)$ was efficiently computed with the recursive residue generation method (RRGM) [13]. The RRGM algorithm employs the Lanczos method to iteratively construct a relatively small tridiagonal matrix representation of the Hamiltonian. The number of Lanczos recursion steps required for convergence ranged from 700 to 2500, depending on the coupling strength. The QR algorithm was then used to extract the residues and eigenvalues from this tridiagonal matrix. The survival probabilities were calculated for all 252 initial conditions, to obtain $P(t) = \langle S(t)\rangle$ [19].

To compute $R(t)$, a different and more computationally expensive procedure was followed. The amplitudes were evaluated by expanding the propagator in Chebyshev polynomials [14], with about 40–440 expansion terms, depending on the time step. The total time range ΔT varied between 10 fs and 125 ps, depending on the coupling strength. Because of the computational expense, the wave function extents were calculated for a representative subset of 18 randomly chosen initial conditions, to obtain $L(t) = \langle R(t)\rangle$ [19].

Figure 1 shows the results of the calculations. The increase in the long time value of $P(t)$ with decreasing coupling strength reveals the influence of the localization transition, as does the large change in the long time value of the average extent of the wave function when the coupling strength changes from just above to below the critical value [20]. Four types of dynamics are exhibited in Fig. 1. First, for strong coupling, cases (a)–(c), a consistent decay of $P(t)$ and increase of $L(t)$ occurs. The decay of $P(t)$ appears linear on the log-log scale for intermediate times. For case (d), the long time values of P and L have started to change. Then, for cases (e)–(g), a partial recurrence, which loses amplitude with decreasing

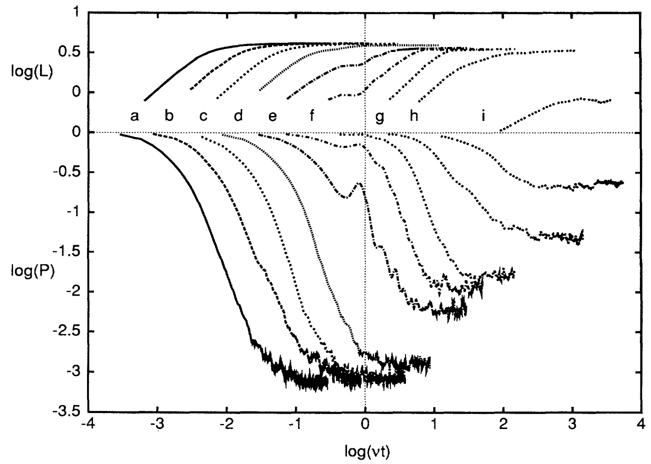

FIG. 1. The average survival probability P and the average wave function extent L as a function of time, on a log-log scale, for different coupling strengths ϕ'. Note that the scale for log(L) is offset by 0.5. The values of $\log(\phi'/\phi'_c)$ are (a) 3.8; (b) 3.3 ; (c) 2.8; (d) 2.3; (e) 1.8; (f) 1.3 ; (g) 0.8 ; (h) 0.3; and (i) –0.2. ν is the harmonic frequency.

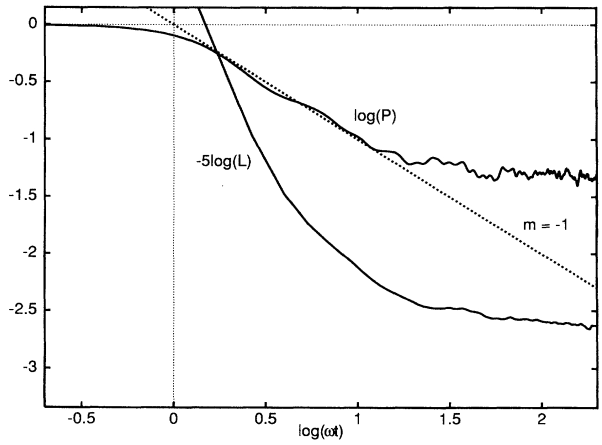

FIG. 2. Diffusional scaling. Shown as a function of time are P, the average survival probability, and L^{-5}, L the average wave function extent, on a log-log scale, for three values of the coupling strength in the strongly delocalized limit, $\log(\phi'/\phi'_c) = 2.8$, 3.3, and 3.8. The power law fit to $P(t)$ appears as a straight line of slope $m = -5/2$. The diffusion coefficient is $D = 11\phi'/\hbar$.

coupling strength, appears in $P(t)$ at roughly $t = 1/\nu$, accompanied by a temporary leveling of $L(t)$. Next, near the transition, for case (h), the decay of $P(t)$, which occurs principally after $t = 1/\nu$, appears linear on the log-log scale for intermediate times, but with a smaller slope than for strong coupling. Finally, on the localized side of the transition, for case (i), the dynamics change dramatically. $L(t)$ always remains less than unity, indicating that the wave function remains almost entirely in the initial state. Also, $P(t)$ in no way reflects the dynamics for individual initial conditions, which are highly oscillatory. In forming the average, these oscillations add incoherently to form a smooth decay of $P(t)$.

Figures 2 and 3 show comparisons of the computational results with the theoretical prediction in the strongly delocalized limit and near the transition, respectively. The model of action diffusion on the surface of constant total energy used in the limit of *strongly delocalized eigenstates*, predicts [4]

$$P(t) \sim L^{-5}(t) \sim (Dt)^{-5/2}, \tag{2}$$

with $5 = s - 1$, the dimensionality of the constant energy surface and $s = 6$ the number of oscillators. *Near the transition to localized eigenstates*, the Schofield-Wolynes scaling analysis gives [4]

$$P(t) \sim L^{-5}(t) \sim (\omega t)^{-1}. \tag{3}$$

Here ω is a microscopic frequency which depends on the local density of states per unit volume. Both power law decays of $P(t)$ are predicted to occur for times when $1 < L < L_{\max}$, with $L_{\max}$ the long time value set by the finite size of the state space. Figures 2 and 3 show clear agreement with the predicted power law decays of $P(t)$ in Eqs. (2) and (3), over 1–1.5 orders of magnitude. Note that although Fig. 3 contains results for several different coupling strengths, all can be fit with the same formula for the diffusion coefficient $D = 11\phi'/\hbar$. This is close to the Logan-Wolynes prediction, $D = 14\phi'/\hbar$ [3,17]. This linear dependence was first seen by Bigwood and Gruebele and confirmed by Ilk, Topaler, and Makri in related calculations which model specific molecules [21]. It contrasts with the quadratic dependence of the decay rate on coupling strength predicted by the golden rule, based on the assumption of weak, global coupling. Note also that for the value of ω used to fit the critical power law decay in Fig. 3, $D/\omega = 1$, using $D = 11\phi'/\hbar$,

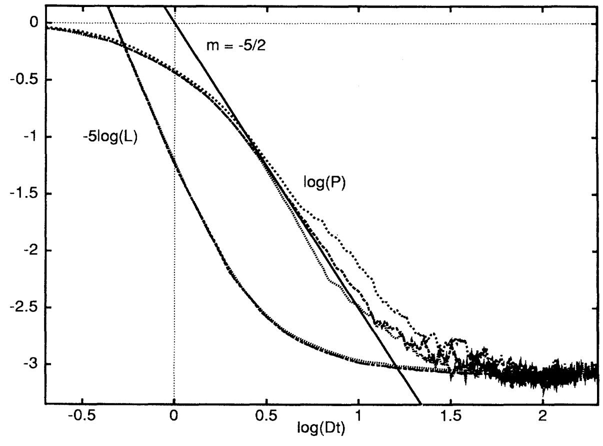

FIG. 3. Critical scaling. Shown as a function of time are P, the average survival probability, and L^{-5}, L the average wave function extent, on a log-log scale, for $\log(\phi'/\phi'_c) = 0.3$. The power law fit to $P(t)$ appears as a straight line of slope $m = -1$. The microscopic frequency is $\omega = 28$ cm $^{-1}$.

the result from the diffusion fit for strong coupling. This reflects the proximity to the localization transition. Figure 2 shows that in the strongly delocalized limit for the same range of time over which $P(t)$ follows the power law decay, it is paralleled by $L^{-5}(t)$, clearly supporting the diffusion picture. That is, agreement is seen with all parts of Eq. (2). Also at long times the equality $P_{\min} = L_{\max}^{-5}$ holds. In contrast, Fig. 3 shows that near the localization transition $P(t)$ and $L^{-5}(t)$ bear no similarity at any time, in disagreement with the first part of Eq. (3). This lack of simple geometrical scaling near the localization transition may reflect multifractal critical eigenstates [22], but further investigation would be necessary to support the connection.

In summary, evidence has been presented for simple dynamical scaling behavior of quantum energy flow for a model system of many anharmonic oscillators with nonlinear local couplings, exhibiting localization as a function of coupling strength. This contrasts with the dynamic localization of kicked rotors [1,12]. Although it is difficult to compare the results to those of classical calculations, due in part to the well-known zero point energy effect [23], preliminary work suggests more rapid classical energy flow. Experiments are, of course, the final desideratum in detecting the scaling behavior of many-dimensional energy flow in molecules. However, so far it has proved difficult to find a tuning parameter, such as the coupling strength in the calculations presented here, in an individual system. In some circumstances external fields or imposed overall rotation could play the role of such tuning. In any event, we believe large scale calculations in combination with scaling ideas are fruitful in uncovering the range of behavior available to individual systems, such as isolated molecules, with anharmonic motions.

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[1] L. E. Reichl, *The Transition to Chaos in Conservative Classical Systems: Quantum Manifestations* (Springer-Verlag, New York, 1992).

[2] S. A. Rice, in *Advances in Laser Chemistry,* edited by A. H. Zewail (Springer, New York, 1978); T. Uzer, Rev. Mod. Phys. **199**, 73 (1991).

[3] D. E. Logan and P. G. Wolynes, J. Chem. Phys. **93**, 4994 (1990).

[4] S. A. Schofield and P. G. Wolynes, J. Chem. Phys. **98**, 1123 (1993).

[5] P. W. Anderson, Phys. Rev. B **36**, 4135 (1958); P. A. Anderson and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[6] E. Abrahams *et al.,* Phys. Rev. Lett. **42**, 673 (1979).

[7] B. V. Chirikov, Phys. Rep. **52**, 263 (1979); D. W. Oxtoby and S. A. Rice, J. Chem. Phys. **65**, 1676 (1976); K. G. Kay, *ibid.* **72**, 5955 (1980); K. M. Atkins and D. E. Logan, *ibid.* **97**, 2438 (1992).

[8] G. A. Voth, R. A. Marcus, and A. H. Zewail, J. Chem. Phys. **81**, 5494 (1984); E. L. Sibert, J. T. Hynes, and W. Reinhardt, J. Phys. Chem. **87**, 2032 (1983); G. A. Voth, J. Chem. Phys. **88**, 5547 (1988); B. Ramachandran and K. G. Kay, J. Chem. Phys. **99**, 3659 (1993), and references therein.

[9] K. M. Atkins and D. E. Logan, Phys. Lett. A **162**, 255 (1992).

[10] A. N. Kaufman, Phys. Rev. Lett. **27**, 376 (1971).

[11] A. J. Lichtenberg and M. A. Leiberman, *Regular and Stochastic Motion* (Springer, New York, 1983).

[12] T. Dittrich and U. Smilansky, Nonlinearity **4**, 59 (1991).

[13] A. Nauts and R. E. Wyatt, Phys. Rev. Lett. **51**, 2238 (1983); R. E. Wyatt, Adv. Chem. Phys. **73**, 231 (1989).

[14] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984); R. Kosloff, *ibid.* **92**, 2087 (1988).

[15] C. Iung and R. E. Wyatt, J. Chem. Phys. **99**, 2261 (1993).

[16] For anisoptropic models showing crossovers between different power law decays, see S. A. Schofield and P. G. Wolynes, J. Phys. Chem. (to be published).

[17] Values used are the site energy distribution width $2\lambda = 26.4\ \mathrm{cm}^{-1}$, the average oscillator excitation level $M = 1.6$, and the average product state connectivity $K = 17$.

[18] P. M. Felker and A. H. Zewail, Adv. Chem. Phys. **70**, 265 (1988); J. D. McDonald, Annu. Rev. Phys. Chem. **30**, 29 (1979).

[19] RRGM and Chebyshev run times increased with decreasing coupling strength and totalled 400 CPU hours on the IBM RS/6000-370 workstation.

[20] The long time values of $S(t)$ varied slightly if the basis set size was increased by letting $v_{\max} = 7$.

[21] R. Bigwood and M. Gruebele, Chem. Phys. Lett. (to be published); G. Ilk, M. Topaler, and N. Makri (unpublished).

[22] H. Grussbach and M. Schreiber, Physica (Amsterdam) **191A**, 394 (1992); U. Fastenrath, M. Janßen, and W. Pook, *ibid.* **191A**, 401 (1992); B. Huckenstein and L. Schweitzer, *ibid.* **191A**, 406 (1992).

[23] W. H. Miller, W. L. Hase, and C. L. Darling, J. Chem. Phys. **91**, 2863 (1989); M. Ben-Hun and R. D. Levine, *ibid.* **101**, 8768 (1994).