Population Diffusion and Equipartition in Quantum Systems of Many Degrees of Freedom

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In the interaction picture, population transfer among coupled degrees of freedom is greatly enhanced by resonances. We show that statistically the number of resonances increases rapidly with degrees of freedom, changing the characteristic of population transfer from being bounded to diffusive. From the diffusion rate we derive simple expressions for the time scales of energy relaxation and equipartition. These expressions are supported by a wide range of experimental data. The analysis elucidates quantitatively the dependence of equipartition on resonances. [S0031-9007(98)05893-1]

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Linearity is one of the most amazing features of quantum mechanics. The spectral decomposition theorem guarantees the existence of a complete orthogonal set of energy eigenstates. In the representation of energy eigenstates, populations of states do not change with time; hence population transfer among genuine eigenstates simply does not occur. However, in practice more often the wave functions of eigenstates are too difficult to solve or use. Therefore, nontrivial quantum dynamic systems are mostly described in the so-called interaction picture, in which the Hamiltonian is decomposed into a solvable major part $\hat{H}_0$ and a minor perturbative part $\hat{V}$. In the interaction picture the physical system is represented by eigenstates of $\hat{H}_0$, which are coupled to each other by $\hat{V}$. In this picture the population changes with time. If $\hat{H}_0$ consists of individually solvable parts representing different degrees of freedom, the population change is interpreted as energy transfer among degrees of freedom.

Energy transfer among a group of coupled states is greatly enhanced when they satisfy the resonance condition $\mathbf{n} \cdot \mathbf{E} \equiv \hbar \Delta\omega \approx 0$, where $\mathbf{n} = (n_1, n_2, \ldots)$ is a nonzero integer array, $\mathbf{E} = (E_1, E_2, \ldots)$ is the energy of the coupled states, and $\Delta\omega$ is the resonance detuning. For a simple system near the ground state, the number of involved energy levels is small, the resonance condition is satisfied only by accident. But in systems of many degrees of freedom where the number of such combinations is large, it would not be a surprise to find many resonances. In this case it is nearly impossible to track the population flow of individual states. Instead, a statistical description of the process is more useful.

Energy transfer in quantum systems has been treated with various models and methods [1]. In many works the general emphasis has been greater on the nonlinear dynamics than on statistical average. Thus, these methods rely heavily on numerical computation to go beyond the mathematical formalism. On the other hand, in a series of recent papers Wolynes, Leitner, and Logan have brought novel approaches to the problem. By modeling multidimensional quantum systems with Cayley trees and analyzing their connectivity with self-consistent solutions of the renormalized Feenberg perturbation series, the authors have addressed important questions such as criterion of quantum ergodicity [2–5], energy relaxation rates [5,6], and probability distribution of the "evenness" of equipartition [7]. In this paper we investigate the problem from a different perspective. Based on the assumption that the relative phases between states are effectively ergodic in the time scale of energy transfer, we study the evolution of the state population rather than the wave function, ignoring any possible phase correlation effects. Using this population-only approach we derived a statistical description of population transfer directly from the quantum equations of motion. For systems of many degrees of freedom, we analyze the probability distribution of resonance detuning and its effect on the population transfer. If all the resonance detunings are sufficiently large, energy could be localized. On the contrary, if there exist sufficiently many resonances of small detuning, a scaling relation between the magnitude of population transfer and its duration can be derived. The relation shows that in such systems population transfer is a diffusion process in the Hilbert space spanned by the eigenfunctions of $\hat{H}_0$. The magnitude of the diffusion rate gives an estimation of the time scale for a system to reach equipartition. The analysis shows how the distribution of resonance detunings dictates energy transfer and equipartition.

To facilitate the discussion, let us use a group of coupled anharmonic oscillators as the model system. The system is general enough that it covers a wide range of physical systems in the real world, from vibration of polyatomic molecules to nonlinear waves. The Hamiltonian has the form $\hat{H} = \hat{H}_0 + \hat{V}$, where the unperturbed part $\hat{H}_0 = \sum_{j=1}^{N} \hbar\omega_j \hat{a}_j^\dagger \hat{a}_j$ is a group of simple harmonic oscillators, and $\hat{V}$ is the interaction Hamiltonian. An arbitrary wave function can be written in the following expansion:

$$\Psi(t) = \sum_{n_1 \cdots n_N} C_{n_1 \cdots n_N}(t) \exp\left(-i \sum_{j=1}^{N} n_j \omega_j t\right) |n_1 \cdots n_N\rangle, \tag{1}$$

where N is the degrees of freedom and n_j the energy level of the jth harmonic oscillator. The equation of motion reads

$$\frac{d}{dt} C_{m_1\cdots m_N}(t) = -\frac{i}{\hbar} \sum_{n_1\cdots n_N} C_{n_1\cdots n_N}(t) \times \exp\left[i \sum_{j=1}^{N} (m_j - n_j)\omega_j t \right] \times V_{m_1\cdots m_N, n_1\cdots n_N}\,, \tag{2}$$

where $V_{m_1\cdots m_N, n_1\cdots n_N} \equiv \langle m_1, \ldots, m_N | \hat{V} | n_1, \ldots, n_N \rangle$. To simplify the notation, let us define $V_{\mathbf{mn}} \equiv V_{m_1\cdots m_N, n_1\cdots n_N}$, $\Delta\omega_{\mathbf{mn}} \equiv \sum_{j=1}^{N} (m_j - n_j)\omega_j$, $C_{\mathbf{m}} \equiv C_{m_1\cdots m_N}$, $C_{\mathbf{n}} \equiv C_{n_1\cdots n_N}$, and $\rho_{\mathbf{nm}} \equiv C_{\mathbf{m}}^* C_{\mathbf{n}}$, where $\Delta\omega_{\mathbf{mn}}$ is the detuning of a particular resonance. In this simplified notation,

$$\frac{d}{dt} \rho_{\mathbf{mm}} = 2\mathrm{Re}\left[-\frac{i}{\hbar} \sum_{\mathbf{n}} \rho_{\mathbf{nm}} V_{\mathbf{mn}} e^{i\Delta\omega_{\mathbf{mn}} t} \right]. \tag{3}$$

Assuming the perturbation is sufficiently weak, so that the change of $\rho_{\mathbf{nm}}$ with time is much slower than that of the phase of the wave functions, one may treat $\rho_{\mathbf{nm}}$ as constants within a short period of observation ΔT and integrate Eq. (3) from t_0 to $t_0 + \Delta T$.

$$\Delta\rho_{\mathbf{mm}} \approx 2\mathrm{Re}\left[\frac{1}{\hbar} \sum_{\mathbf{n}} \frac{\rho_{\mathbf{nm}} V_{\mathbf{mn}}}{\Delta\omega_{\mathbf{mn}}} \times \left(e^{i\Delta\omega_{\mathbf{mn}} t_0} - e^{i\Delta\omega_{\mathbf{mn}} (t_0 + \Delta T)}\right) \right]. \tag{4}$$

Define $\boldsymbol{\rho}$ to be the array of population $\rho_{\mathbf{mm}}$, the total mean square change of $\boldsymbol{\rho}$ is

$$\begin{aligned} |\Delta\boldsymbol{\rho}|^2 &\equiv \sum_{\mathbf{m}} (\Delta\rho_{\mathbf{mm}})^2 \\ &= \frac{4}{\hbar^2} \sum_{\mathbf{m,n}} \frac{|\rho_{\mathbf{nm}} V_{\mathbf{mn}}|^2}{\Delta\omega_{\mathbf{mn}}^2} [1 - \cos(\Delta\omega_{\mathbf{mn}} \Delta T)], \end{aligned} \tag{5}$$

where we have averaged over the starting time t_0. Because $\Delta\omega_{\mathbf{mn}}$ is determined by ω_j from the unperturbed Hamiltonian $\hat{H}_0$, whereas $V_{\mathbf{mn}}$ is determined by the nonlinear perturbation $\hat{V}$, it is reasonable to assume that, in general, the distributions of $\Delta\omega_{\mathbf{mn}}$ and $V_{\mathbf{mn}}$ are independent. Therefore Eq. (5) can be simplified as

$$|\Delta\boldsymbol{\rho}|^2 = \frac{4}{\hbar^2} \left(\sum_{\mathbf{m,n}} |\rho_{\mathbf{nm}} V_{\mathbf{mn}}|^2 \right) \left\langle \frac{1 - \cos(\Delta\omega_{\mathbf{mn}} \Delta T)}{\Delta\omega_{\mathbf{mn}}^2} \right\rangle, \tag{6}$$

where the angle brackets on the right-hand side denote averaging over $\Delta\omega_{\mathbf{mn}}$. In systems of many degrees of freedom the number of possible $\Delta\omega_{\mathbf{mn}}$ is very large. The average can be written as an integral.

$$\left\langle \frac{1 - \cos(\Delta\omega_{\mathbf{mn}} \Delta T)}{\Delta\omega_{\mathbf{mn}}^2} \right\rangle = \int_{|x| \geq |\Delta\omega|_{\min}} \frac{1 - \cos(x\Delta T)}{x^2} \times P(x)\, dx\,, \tag{7}$$

where $P(x)$ is the distribution of $\Delta\omega_{\mathbf{mn}}$, and $|\Delta\omega|_{\min}$ is the lower bound of $\Delta\omega_{\mathbf{mn}}$. In our previous analysis on classical nonlinear systems [8], we have shown that

$$\int_{|x| \geq |\Delta\omega|_{\min}} \frac{1 - \cos(x\Delta T)}{x^2} P(x)\, dx \leq \frac{C}{|\Delta\omega|_{\min} \Omega}\,, \tag{8}$$

where $C \approx 3$ is a constant and Ω is the width of $P(\Delta\omega_{\mathbf{mn}})$. Hence, if $|\Delta\omega|_{\min}$ is not small, meaning the system is far from resonances, $|\Delta\boldsymbol{\rho}|^2$ could be bounded to a near neighborhood of the initial point $\boldsymbol{\rho}$. But, as we shall see, in systems of many degrees of freedom, due to the large number of possible $\Delta\omega_{\mathbf{mn}}$, $|\Delta\omega|_{\min}$ is likely orders of magnitude smaller than Ω. If ΔT is chosen such that $1/\Omega \ll \Delta T \ll 1/|\Delta\omega|_{\min}$, it was shown that [8]

$$\int_{|x| \geq |\Delta\omega|_{\min}} \frac{1 - \cos(x\Delta T)}{x^2} P(x)\, dx \approx \pi P(0) \Delta T\,. \tag{9}$$

Since $\sum_{\mathbf{m,n}} |\rho_{\mathbf{nm}} V_{\mathbf{mn}}|^2 \approx 2(\sum_{\mathbf{m,n}} \rho_{\mathbf{nm}} V_{\mathbf{mn}})^2 = 2\langle\hat{V}\rangle^2$, where $\langle\hat{V}\rangle$ is the expectation value of $\hat{V}$, from Eqs. (6) and (7)

$$|\Delta\boldsymbol{\rho}|^2 \approx \frac{8\pi P(0)}{\hbar^2} \langle\hat{V}\rangle^2 \Delta T\,. \tag{10}$$

The scaling relation between $|\Delta\boldsymbol{\rho}|^2$ and ΔT shown above belongs to that of the random walk, and thus establishes the diffusive character of the population transfer with diffusion rate $D = 8\pi P(0) \langle\hat{V}\rangle^2/\hbar^2$.

Thus, it is clear that the magnitude of $|\Delta\omega|_{\min}$ determines the character of the population transfer process. Diffusion dominates when there exist sufficiently many resonances of small detuning. This is highly probable in large systems. It should be noted that here the choice of the coarse graining parameter ΔT is important. If ΔT is too small, the correlation between consecutive points in time is so strong that one falls back to the equation of motion, whereas if ΔT is too large, one may not be able to deduce a useful correlation. Only in the appropriate time scale $1/\Omega \ll \Delta T \ll 1/|\Delta\omega|_{\min}$ the diffusive character is exposed.

We have clarified the relation between resonance and population diffusion, and derived a simple expression for the diffusion rate. Now we shall refine the theory to give an account on how to calculate $|\Delta\omega|_{\min}$ from $P(\Delta\omega_{\mathbf{mn}})$. In order to do so, we shall first decompose the interaction Hamiltonian according to the order of interaction.

$$\hat{V} = \sum_{q=3}^{\infty} \hat{V}_q = \sum_{q=3}^{\infty} \sum_{o(\mathbf{l})=q} V_{l_1,\ldots,l_N} \prod_{j=1}^{N} r_j^{l_j}\,, \tag{11}$$

where each r_j is one of the canonical variables of the jth degree of freedom, and $o(\mathbf{l}) \equiv \sum_{j=1}^{N} l_j$ is the order of interaction. If all the $|\Delta\omega_q|_{\min} \equiv \min_{o(\mathbf{m})+o(\mathbf{n})=q} |\Delta\omega_{\mathbf{mn}}|$ are sufficiently small,

$$|\Delta\boldsymbol{\rho}|^2 = \sum_{q=3}^{\infty} \frac{8\pi P_q(0)}{\hbar^2} \langle\hat{V}_q\rangle^2 \Delta T\,, \tag{12}$$

where $P_q(x)$ is the probability distribution of $\Delta\omega_{\mathbf{mn}}$ with $o(\mathbf{m}) + o(\mathbf{n}) = q$. It can be shown by probability analysis [8] that

$$\langle |\Delta\omega_q|_{\min} \rangle \approx \frac{1}{2^q C_q^N P_q(0)}\,, \tag{13}$$

where $\langle |\Delta\omega_q|_{\min} \rangle$ is the expectation value of $|\Delta\omega_q|_{\min}$ and N the degrees of freedom. Because for $q \ll N$, $\langle |\Delta\omega_q|_{\min} \rangle$ decreases rapidly with increasing q, it appears that diffusion occurs more likely for higher order interactions. However, it should be noted that $\langle\hat{V}_q\rangle$ also decrease rapidly with increasing q. Therefore, although it is true that the contribution of high order interactions to $|\Delta\boldsymbol{\rho}|^2$ is more likely in the form of population diffusion, the corresponding diffusion rate $D_q = 8\pi P_q(0)\langle\hat{V}_q\rangle^2/\hbar^2$ is not necessarily large enough to bear any practical significance. Under the general condition that D_q decreases rapidly with q, it is seen that the dominant contribution to the diffusion rate comes from the smallest q for which $|\Delta\omega_q|_{\min}$ is small enough that a coarse graining time scale ΔT satisfying $1/\Omega_q \ll \Delta T \ll 1/|\Delta\omega_q|_{\min}$ can be found.

The scaling relation of $|\Delta\omega_q|_{\min}$ in Eq. (13) reveals that it does not take a large N to make the population transfer diffusive. Let us require $|\Delta\omega_q|_{\min} \leq 10^{-4}\Omega$ to leave plenty of room for the choice of ΔT, and note that for even q, the peak of $P_q(\Delta\omega_q)$ is at $\Delta\omega_q = 0$, therefore $P_q(0)\Omega \approx 1$. For $q = 4$ the requirement is $N \geq 13$. In the case of vibrational degrees of freedom of polyatomic molecules, it means the molecule is larger than 5 atoms. This simple calculation explains why statistical theories (such as the Rice-Ramsperger-Kassel-Macus theory) work well in predicting the unimolecular reaction rates and the energy distribution of the products for molecules larger than 5 atoms [9]. It has been a surprise that statistical mechanics can be applied to systems of so few degrees of freedom. Yet from our analysis, it is seen that when the internal energy is large enough to make the coupling between degrees of freedom significant, as is the case for highly excited molecules, rapid population diffusion is anticipated. The population diffusion can render the molecule ergodic before reactions take place, justifying the application of statistical mechanics.

The relation between population diffusion and resonances deciphered above reinforces the common notion that resonances are the foundation of the ergodicity or equipartition postulate. Yet, in the practical world whether equipartition occurs depends on the time scale T_e for the system to reach equipartition. After clarifying the distinctively different roles of resonances from nonlinear coupling, we are in a good position to estimate T_e. Consider the expectation value of $\hat{H}_0$.

$$\langle\hat{H}_0\rangle = \sum_{\mathbf{n}} \rho_{\mathbf{nn}} H_{0_{\mathbf{nn}}} = \sum_{\mathbf{n}} \left(\rho_{\mathbf{nn}} \sum_{j=1}^{N} n_j \hbar\omega_j \right) \approx N\hbar\bar{\omega}\bar{n}\,, \tag{14}$$

where $\bar{\omega} \equiv \sum_{j=1}^{N} \omega_j/N$ is the average frequency of the oscillators and $\bar{n} \equiv \sum_{\mathbf{n}} o(\mathbf{n})\rho_{\mathbf{nn}}/N$ is the average quantum number per mode. In the classical limit, $\hbar\bar{n}$ corresponds to the average action per degree of freedom. Let us define T_e to be the time for the diffusion to make $|\Delta\boldsymbol{\rho}|$ twice as large as a typical root-mean-square distance $\overline{|\boldsymbol{\rho}|} = \sqrt{N\bar{n}^2}$, so that at $t = T_e$ most of the $\boldsymbol{\rho}$ space is filled up by population diffusion. From Eq. (12) and Eq. (14)

$$\frac{1}{T_e} \equiv \frac{\sum_q D_q}{(2\overline{|\boldsymbol{\rho}|})^2} \approx \frac{2\pi N\bar{\omega}^2 \sum_q P_q(0)\langle\hat{V}_q\rangle^2}{\langle\hat{H}_0\rangle^2}\,. \tag{15}$$

The expression of T_e above is the same as that for classical nonlinear systems [8]. Its accuracy has been verified by large scale numerical simulations. In the energy range where the perturbation treatment is valid, the ratio $\langle\hat{V}_q\rangle^2/\langle\hat{H}_0\rangle^2$ decreases rapidly with q, meaning that it takes a much longer time for high order interactions to cause equipartition, even though for them $|\Delta\omega_q|_{\min}$ is smaller. It is also important to note that T_e depends on the choice of $\hat{H}_0$. The closer $\hat{H}_0$ is to the full Hamiltonian, the smaller $\langle\hat{V}\rangle^2/\langle\hat{H}_0\rangle^2$. Therefore, in discussing the energy relaxation or equipartition problem one must specify the basis set as well as the way energy is deposited initially. Ambiguity in these respects has long been a source of controversy.

It might seem strange that Eq. (15) does not depend on $\hbar$, given that it is derived directly from quantum equations of motion. This is because for systems with many coupled degrees of freedom the diffusion rate and the volume of the $\boldsymbol{\rho}$ space to be filled up are both proportional to $1/\hbar^2$. The dependence on $\hbar$ thus cancels. However, $\langle\hat{V}_q\rangle^2/\langle\hat{H}_0\rangle^2$ may depend on $\hbar$ implicitly, depending on how other parameters (average energy, frequency, spring constant, equivalent mass) are scaled with $\hbar$.

Despite its formal similarity to Fermi's golden rule, Eq. (15) is much more general and carries much more information. The golden rule is derived under the condition that the population of the initial state is not appreciably depleted, thus it is not valid beyond the short time limit. In Eq. (15) the roles of degrees of freedom and average energy in equipartition are apparent, whereas the golden rule only gives the initial energy relaxation rate of a particular energy eigenstate, not the equipartition time scale that depends on average energy and degrees of freedom. Nor does the golden rule tell whether the population transfer will be bounded, as in, e.g., multiple quantum beats. By focusing on the statistical dynamics and its scaling laws in the $\boldsymbol{\rho}$ space, as opposed to the energy relaxation rate of a single state, we have derived a much more useful equation.

As a demonstration of the usefulness of Eq. (15), let us treat the problem of intramolecular vibrational energy redistribution. The problem has attracted much interest since the discovery that molecules can be dissociated by absorbing many infrared photons in the electronic ground state [10]. It was hoped that mode-selective photochemistry can be done by use of high-power infrared lasers. However, it was soon realized that energy in the pumped mode quickly leaks into other modes. Therefore it is crucial to excite the molecules faster than the time scale of energy relaxation T_r. Determining T_r by experiments has been more difficult than one might expect. In the time domain, lack of a high-power tunable ultrashort-pulse infrared laser limited the energy range and molecular species of the experiments [11]. On the other hand, early frequency-domain experiments suffered from inhomogeneous broadening. Unambiguous measurements on homogeneous linewidths of vibrational states in diverse cases were reported only recently [12–16]. As we shall see, these measurements provide direct tests of our theory.

For practical purposes the energy levels of a vibrational mode near the ground state can be written as

TABLE I. Comparison with experimental data.

Molecule	Internal energy (cm^{-1})	$\bar{n}$	$\bar{\omega}$ (cm^{-1})	T_r or $\frac{1}{4\pi T_r c}$	Experimental data
SF_6	4000	0.42	631	0.40 cm^{-1}	0.25 cm^{-1} [13]
SF_6	4253	0.45	631	5.9 ps	11 ps [11]
SF_6	11 500	1.2	631	3.3 cm^{-1}	3 cm^{-1} [12]
SF_6	17 000	1.8	631	7.2 cm^{-1}	5 cm^{-1} [12]
SF_6	32 000	3.4	631	25 cm^{-1}	12 cm^{-1} [12]
SF_6	34 000	3.6	631	29 cm^{-1}	15 cm^{-1} [13]
CF_3I	5360	0.88	676	0.67 cm^{-1}	1 cm^{-1} [14]
CF_3I	10 720	1.8	676	2.7 cm^{-1}	5 cm^{-1} [14]
CF_3I	19 000	3.1	676	8.4 cm^{-1}	5 cm^{-1} [15]
C_6H_6	5186	0.12	1464	9.2 ps	7.6 ps [16]
C_6H_6	8165	0.19	1464	3.7 ps	6.2 ps [16]
C_6H_6	9158	0.2	1464	2.9 ps	3.6 ps [16]

$E(n) = n\hbar\omega + n^2 x$, where x is the anharmonicity constant. For medium-sized molecules, $x/(\hbar\omega)$ is typically $\approx$0.5%, therefore $\langle\hat{V}\rangle^2/\langle\hat{H}_0\rangle^2 \approx (0.005\bar{n})^2$. Because the width of the distribution of vibrational frequency is about as large as the average frequency itself, from the central limit theorem $P(0) \approx 0.2/\bar{\omega}$ for low order interactions [8]. Hence, in a rough sense the only variable in Eq. (15) is $\bar{n}$, which is just the total vibrational energy divided by $N\hbar\bar{\omega}$. Note that because it should take a considerably longer time for the population to diffuse to the entire $\boldsymbol{\rho}$ space than just diffusing out of a pumped mode, it is reasonable to postulate that T_e/T_r is just the ratio of the typical mean square distances, $N\bar{n}^2$ and $\bar{n}^2$, respectively, in the two cases. Hence

$$\frac{1}{T_r} \approx 2\pi N^2 \bar{\omega} \times 0.2 \times (0.005\bar{n})^2. \qquad (16)$$

Comparison of Eq. (16) with experiments is shown in Table I. T_r is related to γ, the measured half-width-at-half-maximum of the resonance spectrum, by $1/T_r = 4\pi\gamma$. It is seen that experimental data agree with Eq. (16) to within a factor of 2. Considering that minimal information is required to use Eq. (16), and that no fitting parameter is involved, the agreement is remarkable.

In conclusion, our analysis points out that, when the perturbation is weak, resonance plays a dominant role in determining whether or not a system will reach equipartition, whereas the magnitude of coupling strength, or equivalently the internal energy, determines the time scale for that to happen. This explains why, in general, statistical mechanics works well in systems of many degrees of freedom, whether or not their internal energy is large enough to make the coupling between degrees of freedom significant. It also explains why statistical mechanics works in nonchaotic systems, such as lattice vibration at low temperature.

Our analysis also explains why the microcanonical ensemble can be constructed in the Schrödinger picture. Since there is no population transfer in the Schrödinger picture, how can the ensemble average be relevant? The fact is that as long as there is any tiny, high order perturbation left out from the unperturbed Hamiltonian, there can be no ideal Schrödinger picture. For systems of a few coupled degrees of freedom, the effect of such tiny perturbation is indeed negligible, because the population transfer is bounded to a small region in the $\boldsymbol{\rho}$ space. However, in systems of many coupled degrees of freedom, even tiny perturbations cause population diffusion. Therefore, in the long run the partition function becomes valid.

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