INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **34** (2001) 11149–11166 PII: S0305-4470(01)28617-X

Energy-shell bases

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Received 7 September 2001
Published 30 November 2001
Online at stacks.iop.org/JPhysA/34/11149

Abstract

A new type of basis set for quantum mechanical problems is introduced. These basis states are adapted to describing the dynamics of a Hamiltonian $\hat{H}$ which is dependent upon a parameter X. A function $f(E)$ is defined which is an analytic function of E, and which is negligibly small when $|E| \gg \delta E$, where δE is large compared to the typical level separation. The energy-shell basis set consists of states $|\xi_n(X)\rangle$ which are derived by applying the operator $f(\hat{H}(X) - \bar{E}_n(X))$ to elements of a fixed basis set, where $\bar{E}_n(X)$ is an analytic approximation to an eigenvalue $E_n(X)$. The energy-shell basis states are combinations of states close to energy E_n, but vary more slowly as a function of X than the eigenfunctions $|\phi_n(X)\rangle$ of $\hat{H}(X)$. This feature gives the energy-shell basis states some advantages in analysing solutions of the time-dependent Schrödinger equation.

PACS numbers: 03.65.-w, 02.10.Yn, 05.45.Mt

1. Introduction

1.1. Commonly used representations of quantum dynamics

Many quantum mechanical experiments involve probing a system with an externally applied disturbance, and observing the response. The Hamiltonian $\hat{H}$ of the system depends on a parameter X, which describes the effect of the external perturbation, and which is itself a function of time. The full solution of the problem is described by the evolution operator $\hat{U}(t, t_0)$, which gives the wavefunction $|\psi(t)\rangle$ at time t from that at the earlier time t_0:

$$|\psi(t)\rangle = \hat{U}(t, t_0)|\psi(t_0)\rangle. \tag{1.1}$$

The evolution operator satisfies the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\, \partial_t \hat{U}(t, t_0) = \hat{H}(X(t))\, \hat{U}(t, t_0) \tag{1.2}$$

with the initial condition $\hat{U}(t_0, t_0) = \hat{I}$, the identity operator.

It is usually natural to expand the wavefunction as a combination of a complete orthonormal set of discrete states, $|\chi_n\rangle$, which may depend upon the parameter X

$$|\psi(t)\rangle = \sum_n a_n(t)\ \exp[-\mathrm{i}\theta_n(t)]\,|\chi_n(X(t))\rangle. \tag{1.3}$$

The phase $\theta_n(t)$ may be chosen to simplify the equation of motion of the coefficients $a_n(t)$. This paper will be concerned with making an appropriate choice of the states $|\chi_n(X)\rangle$ in order to facilitate finding approximate solutions of the Schrödinger equation. Substituting (1.3) into the Schrödinger equation leads to an equation of motion for the coefficients $a_n(t)$ of the form

$$\mathrm{i}\hbar\,\dot{a}_n = \sum_m \mathcal{H}_{nm}(t)\ \exp\left[\mathrm{i}\big(\theta_n(t) - \theta_m(t)\big)\right] a_m \tag{1.4}$$

where $\dot{f} \equiv \mathrm{d}f/\mathrm{d}t$, and

$$\mathcal{H}_{nm}(t) = \left[\langle\chi_n(X)|\hat{H}(X)|\chi_m(X)\rangle - \delta_{nm}\hbar\partial_t\theta_n(t)\right] - \mathrm{i}\hbar\dot{X}\langle\chi_n(X)|\partial_X\chi_m(X)\rangle. \tag{1.5}$$

The matrix with elements $\mathcal{H}_{nm}(t)$ is Hermitean. It contains a component which depends only upon X, and a term which is proportional to the velocity $\dot{X}$. It will be written

$$\mathcal{H}_{nm} = H_{nm}(X) + \mathrm{i}\hbar\dot{X}\mathcal{Z}_{nm}(X) \tag{1.6}$$

where the elements $\mathcal{Z}_{nm}(X)$ are antiHermitean: $\mathcal{Z}^*_{mn} = -\mathcal{Z}_{nm}$.

I shall now describe two commonly used basis sets, and discuss reasons for introducing alternative choices. In many situautions the parameter $X(t)$ remains bounded, with its deviation from X_0 remaining small. In these cases it is convenient to expand the wavefunction in the terms of the eigenfunctions of the Hamiltonian, satisfying

$$\hat{H}(X)|\phi_n(X)\rangle = E_n(X)|\phi_n(X)\rangle \tag{1.7}$$

and the eigenfunctions $|\phi_n(X_0)\rangle$ would be a suitable choice for the basis set in (1.3). Using a time-independent basis is termed using a 'fixed basis set', and a fixed basis consisting of eigenfunctions is a convenient choice. Also, it is natural to take $\theta_n(t) = E_n(X_0)t/\hbar$, which makes the diagonal elements H_{nn} equal to zero. In this case the terms in (1.6) containing $\mathcal{Z}_{nm}$ vanish. The first term can be expanded as Taylor series in $X(t)$. Truncating at the leading order term gives (for $n \neq m$)

$$\mathcal{H}_{nm} = (\partial_X H)_{nm}(X_0)\ \exp\left[\mathrm{i}(E_n - E_m)t/\hbar\right][X(t) - X_0] \tag{1.8}$$

where $(\partial_X H)_{nm}$ are matrix elements of $\partial\hat{H}/\partial X$ evaluated in the basis formed by the eigenfunctions

$$(\partial_X H)_{nm}(X) = \left\langle \phi_n(X) \left| \frac{\partial\hat{H}}{\partial X} \right| \phi_m(X) \right\rangle. \tag{1.9}$$

This approach of using a fixed basis set has the disadvantage that the matrix elements $\mathcal{H}_{nm}$ can become large if the perturbation does not remain small.

If the parameter $X(t)$ undergoes a large excursion, it may be possible to obtain a more convenient representation of the Schrödinger equation by using parameter-dependent basis states. If the parameter $X(t)$ varies very slowly, and the adiabatic basis, formed by the instantaneous eigenstates of the Hamiltonian, is preferred. The quantum adiabatic principle [1] shows that, if the Hamiltonian varies sufficiently slowly, a particle initially in the nth adiabatic state $|\phi_n(X_0)\rangle$ remains close to the nth state, such that the state at time t is approximately $\exp[\mathrm{i}\Theta(t)]|\phi_n(X(t))\rangle$ (for some phase angle $\Theta(t)$). This adiabatic basis is therefore expected to give a very efficient representation of the dynamics when $\dot{X}$ is small. The phases θ_n are chosen to be integrals of the energies, so that the following substitutions are made in (1.3):

$$|\chi_n(X)\rangle = |\phi_n(X)\rangle \qquad \theta_n(t) = \frac{1}{\hbar}\int^t \mathrm{d}t'\ E_n(X(t')). \tag{1.10}$$

In this basis, the diagaonal elements $\mathcal{H}_{nn}$ vanish, and the off-diagonal matrix elements are

$$\mathcal{H}_{nm}(t) = \mathrm{i}\hbar\dot{X}\exp\left[\mathrm{i}(\theta_n(t) - \theta_m(t))\right]\frac{(\partial_X H)_{nm}(X)}{E_n(X) - E_m(X)}. \tag{1.11}$$

The diagonal matrix elements are made equal to zero by choosing the phases of the states $|\phi_n(X)\rangle$ so that $\langle\partial_X\phi_n|\phi_n\rangle = 0$. The adiabatic basis is an efficient representation when $\dot{X}$ is sufficiently small.

The matrix elements $\mathcal{Z}_{nm}$ in (1.6) are zero when a fixed basis is used, and the H_{nm} are zero when the adiabatic basis is used. In general, both terms are present, but for a sufficiently large value of $|\dot{X}|$ the H_{nm} may be negligible. This latter case will be of most interest here.

1.2. Motivation for introducing energy-shell bases

It has already been remarked that the fixed state basis is not ideal when the excursion of $X(t)$ is large. A difficulty also arises with the adiabatic representation, in that the matrix elements $(\partial_X H)_{nm}$ are very rapidly varying functions of the parameter X, because the adiabatic states are very sensitive to changing the parameter X. This feature makes it difficult to obtain predictions from the adiabatic representation when $\dot{X}$ is larger than a certain characteriztic value [2]. This characteriztic value is small compared to values required for many applications, making it desirable to find a set of basis states which evolves as the parameter X changes, but which are not as sensitive to changes of the parameter as the adiabatic states. It is natural to define a set of states $|\chi_n(X)\rangle$ which are combinations of the adiabatic states in a small interval of energy, of size δE. This interval is centred on $\bar{E}_n(X)$, which is an analytic approximation to $E_n(X)$. The states $|\chi_n(X)\rangle$ are defined so that they vary much more slowly than the eigenfunctions as a function of X. A set of states having this property is defined in section 2. It will be termed the energy-shell basis.

If the exact values of the matrix elements $\mathcal{H}_{nm}(X, \dot{X})$ can be evaluated, then (1.5) is an exact representation of the Schrödinger equation. In most of the potential applications of this approach, the Hamiltonian would be a 'complex' quantum system, for which it would be impossible to obtain analytic expressions for the matrix elements. The matrix elements could either be evaluated numerically, or else they could be characterized statistically, and the Schrödinger equation would then be modelled by a system of stochastic differential equations, in which the matrix elements $\mathcal{H}_{nm}(X, \dot{X})$ are replaced by random functions with the same statistical properties. This approach has been described in [2] for the special case where the adiabatic basis is used. It is adequate when statistical properties of the evolution operator, rather than accurate estimates of individual matrix elements, are required. The remaining sections of the paper will be concerned with this statistical approach. Section 3 will consider estimates for the variance of the matrix elements $\mathcal{H}_{nm}$, and section 4 will consider their correlation functions.

These estimates will be given in terms of two parameters characterizing the Hamiltonian, namely the average density of states, ρ, and the typical size σ of the matrix elements (1.9). The latter quantity is a function of the energy difference $\Delta E = E_n - E_m$, and of the mean energy $E = \frac{1}{2}(E_n + E_m)$, and is defined in terms of a second moment as follows:

$$\sigma^2(\Delta E, E) = \frac{1}{\rho^2}\sum_{n,m\neq n}|(\partial_X H)_{nm}|^2\delta_\varepsilon(\Delta E - E_n + E_m)\,\delta_\varepsilon\left(E - \tfrac{1}{2}(E_n + E_m)\right). \tag{1.12}$$

Here $\delta_\varepsilon(E)$ is a broadened delta function, with support ε and weight equal to unity. The support is chosen so that $\varepsilon\rho \gg 1$, implying that many elements contribute to (1.12), but ε is small compared to all of the other energy scales involved. The dependence of σ^2 on E will not be made explicit, and this quantity will subsequently be written $\sigma^2(\Delta E)$. This function is

assumed to be non-zero at $\Delta E = 0$ and to decay rapidly as $|\Delta E| \to \infty$ when ΔE exceeds a characteriztic size ΔE_c. It will be characterized by two numbers, namely a typical magnitude $\sigma_0^2 = \sigma^2(0)$ and its 'support' ΔE_c. The energy scale ΔE_c is often referred to as the correlation energy, because in systems which exhibit chaotic classical behaviour it is reciprocal to the timescale τ_c for the decay of correlations of classical observables: $\Delta E_c = \hbar/\tau_c$.

1.3. Energy diffusion and dissipation

The evolution operator can be described in terms of matrix elements in an energy-shell basis, formed by states $|\chi_n(X)\rangle$:

$$\mathcal{U}_{nm}(t, t_0) = \langle \chi_n(X(t))|\hat{U}(t, t_0)|\chi_m(X(t_0))\rangle. \tag{1.13}$$

The matrix element $\mathcal{U}_{nm}(t, t_0)$ is the amplitude to the reach state with index n at time t, having started in a state with index m at time t_0. These elements can be characterized statistically in terms of moments of the transition probability $|\mathcal{U}_{nm}|^2$. The second moment

$$\Delta(t) = \sum_n \left\langle |\mathcal{U}_{nm}(t, t_0)|^2 (\bar{E}_n - \bar{E}_m)^2 \right\rangle \tag{1.14}$$

(where the angle brackets indicate an average over the initial state, indexed by m) will be considered in section 5. In the case where the adiabatic basis is used [2], it has been argued that this quantity exhibits linear growth, indicating a diffusive spread of the energy of a particle:

$$\frac{\mathrm{d}\Delta(t)}{\mathrm{d}t} = 2D_E(\dot{X}). \tag{1.15}$$

The same argument applies to the more general energy shell bases which are considered here. The diffusion constant D_E is estimated in section 5, using a perturbative method.

It has also been argued that the diffusion constant is proportional to the rate of dissipation of energy. In systems of independent fermions at low temperatures, the formula for the rate of dissipation takes a particularly simple form [3]:

$$\frac{\mathrm{d}E_T}{\mathrm{d}t} = \rho D_E, \tag{1.16}$$

where E_T is the total energy absorbed by the reservoir of fermions, and where both ρ and D_E are evaluated at the Fermi energy.

The usual approach to calculating the rate of dissipation is via the Kubo formula [4], which is a pertubative expression. The version of the Kubo formula appropriate to the independent particle model was given by Greenwood [5], and will be termed the Kubo–Greenwood formula. The rate of dissipation obtained from (1.16) agrees with the Kubo–Greenwood formula in the limits temperature $T \to 0$ and frequency $\omega \to 0$ if

$$D_E = \pi\hbar\rho\sigma_0^2\dot{X}^2. \tag{1.17}$$

In [2], which used the adiabatic basis, it was argued that the diffusion constant is given by (1.17) provided $|\dot{X}|$ is smaller than some limiting value $\dot{X}_{\max}$. The use of the energy-shell bases, together with some additional assumptions which will be described later, justify a much larger value of $\dot{X}_{\max}$. The conclusions about the validity of (1.17) are discussed in section 6. The value of $\dot{X}_{\max}$ obtained there is still not an optimal estimate for many systems.

In this paper no systematic attempt is made to consider the errors introduced by the various approximations which must be used. The symbol $A \approx B$ means that A and B are approximately equal, and $A \sim B$ means that A/B is a number of order unity.

2. Energy-shell bases

2.1. Quasi-projection onto the energy shell

The definition of the energy-shell basis requires an analytic function of energy, $f(E)$, an analytic approximation to the energy of the state with index n, which will be denoted $\bar{E}_n(X)$, and a set of states with elements $|\alpha_n\rangle$.

The function $f(E)$ is positive, and has significant magnitude in an interval of width δE, centred on zero. An example of such a function would be

$$f(E) = A \exp\left[-E^2/2\delta E^2\right] \tag{2.1}$$

where A is a constant.

The function $\bar{E}_n(X)$ is a smooth function of X chosen so that the energy of the nth state of the system is close to $\bar{E}_n(X)$. If the system has a classical limit, with d degrees of freedom, this requirement is satisfied by requiring that the volume of the energy shell remains equal to n times the phase-space volume per state which is expected from the Weyl rule, namely h^d [6]. If $\Omega(E, X)$ is the phase-space volume inside an energy shell at E, the following equations give an implicit definition of $\bar{E}_n(X)$:

$$\Omega(\bar{E}_n(X), X) = n(2\pi\hbar)^d \qquad \Omega(E, X) = \int \mathrm{d}\boldsymbol{q} \int \mathrm{d}\boldsymbol{p}\, \Theta(E - H(\boldsymbol{q}, \boldsymbol{p}, X)). \tag{2.2}$$

(Here $\Theta(x)$ is the Heaviside function, $\Theta(x < 0) = 0$, $\Theta(x \geqslant 0) = 1$.) The function $\Omega(E, X)$ also provides an estimate of the density of states:

$$\rho(E, X) = \frac{1}{(2\pi\hbar)^d} \frac{\partial \Omega}{\partial E}\bigg|_{E,X}. \tag{2.3}$$

If no classical limit exists, alternative definitions of ρ and $\bar{E}_n$ can be used. For example, $\bar{E}_n(X)$ could be obtained by numerically smoothing away the fluctuations of the actual eigenvalues, $E_n(X)$.

It will also be assumed that a set of orthonormal states with elements $|\alpha_n\rangle$ are available, which are independent of X:

$$\langle\alpha_n|\alpha_m\rangle = \delta_{nm}. \tag{2.4}$$

The states $|\alpha_n\rangle$ are highly arbitrary, and the minimal requirements they must satisfy will be discussed later.

A set of states with elements $|\xi_n(X)\rangle$ can be generated using the function $f(E)$ as follows:

$$|\xi_n(X)\rangle = f\big(\hat{H}(X) - \bar{E}_n(X)\big)\,|\alpha_n\rangle. \tag{2.5}$$

Functions of the Hamiltonian are defined in terms of the eigenfunctions and eigenvalues:

$$f(\hat{H}) = \sum_n |\phi_n\rangle f(E_n) \langle\phi_n| \tag{2.6}$$

where the sum runs over all of the eigenfunctions $|\phi_n\rangle$. The set of states with elements $|\xi_n(X)\rangle$ is termed the energy-shell basis.

If $f(E)$ took the value unity when E is close to zero, and was equal to zero elsewhere, then the states $|\xi_n(X)\rangle$ would represent a projection onto the energy shell of the Hamiltonian at energy $\bar{E}_n(X)$. Such a projection would fluctuate as rapidly as the eigenstates $|\phi_n(X)\rangle$. The use of the analytic function $f(E - \bar{E}_n)$ to select states in the neighbourhood of $\bar{E}_n(X)$ can be termed a 'quasi-projection' onto the 'energy shell'. The motivation for using an analytic function is that the energy-shell basis states are expected to fluctuate less rapidly than the eigenstates.

The eigenstates decorrelate on a scale $\delta X_0 \sim (\rho\sigma_0)^{-1}$, whereas the Hamiltonian is assumed to decorrelate when X changes by an amount of order unity. The operator $f(\hat{H} - \bar{E}_n)$ is expected to decorrelate more rapidly than the Hamiltonian, but less rapidly than the eigenfunctions (provided $\rho\delta E \gg 1$). A calculation (based upon random matrix models) of the scale $\delta X_{\delta E}$ over which the states $|\xi_n(X)\rangle$ decorrelate is given in section 4.

2.2. *Orthogonalization of the basis set*

The states $|\xi_n(X)\rangle$ do not form an orthonormal set. It is useful to define matrix elements of a 'normalization operator' as follows:

$$N_{nm} = \langle \xi_n | \xi_m \rangle. \tag{2.7}$$

The constant A in (2.1) will be chosen so that

$$\langle N_{nn} \rangle = 1 \tag{2.8}$$

where the angle brackets denote an average over states. This average will be expressed in terms of the quantity

$$\langle |\langle \phi_j | \alpha_n \rangle|^2 \rangle = p(E_j - \bar{E}_n). \tag{2.9}$$

Here the angle brackets denote an average over the state labels j and n, with only states with a given value of $E_j - E_n$ being included: this average can be defined by an expression analogous to (1.12). It will be assumed that $p(E)$ is a smooth function which is negligible when $|E| \gg \Delta E_\alpha$, with $\Delta E_\alpha \gg \delta E$. The fact that the $|\alpha_n\rangle$ are normalized implies that

$$1 = \sum_j \langle |\langle \phi_j | \alpha_n \rangle|^2 \rangle \approx \rho \int_{-\infty}^{\infty} \mathrm{d}E \; p(E). \tag{2.10}$$

Now, requiring that (2.8) is satisfied leads to

$$\begin{aligned} 1 = \langle\langle \xi_n | \xi_n \rangle\rangle &= \sum_j \langle |\langle \alpha_n | \phi_j \rangle|^2 \rangle f^2(E_j - \bar{E}_n) \\ &\approx \rho \int_{-\infty}^{\infty} \mathrm{d}E \; p(E) f^2(E) \approx \rho \, p(0) \int_{-\infty}^{\infty} \mathrm{d}E \; f^2(E) \end{aligned} \tag{2.11}$$

where it has been assumed that the coefficients $\langle \phi_j | \alpha \rangle$ are uncorrelated, and the final approximation uses $\Delta E_\alpha \gg \delta E$. Equations (2.10) and (2.11) represent normalization requirements on the functions f and p. In the case where the function $f(E)$ is given by (2.1), (2.11) becomes $\sqrt{\pi} A^2 \rho p(0) \delta E = 1$.

It is instructive to estimate the mean-squared value for the off-diagonal elements of the normalization matrix:

$$\begin{aligned} \langle |N_{nm}|^2 \rangle = \Bigg\langle & \sum_j \sum_{j'} \langle \alpha_n | \phi_j \rangle f(E_j - \bar{E}_n) f(E_j - \bar{E}_m) \langle \phi_j | \alpha_m \rangle \\ & \times \langle \alpha_m | \phi_{j'} \rangle f(E_{j'} - \bar{E}_n) f(E_{j'} - \bar{E}_m) \langle \phi_{j'} | \alpha_n \rangle \Bigg\rangle \\ \approx & \sum_j \langle |\langle \alpha_n | \phi_j \rangle|^2 \rangle \langle |\langle \alpha_m | \phi_j \rangle|^2 \rangle f^2(E_j - \bar{E}_n) f^2(E_j - \bar{E}_m) \\ \approx & \rho p^2(0) \int_{-\infty}^{\infty} \mathrm{d}E \; f^2(E) f^2(E + \bar{E}_n - \bar{E}_m). \end{aligned} \tag{2.12}$$

It has been assumed that the coefficients $\langle\phi_j|\phi_n\rangle$ and $\langle\phi_{j'}|\phi_n\rangle$ are statistically independent when $j \neq j'$. Equation (2.11) gives the estimate $\rho p(0)\delta E f^2(0) \sim 1$, implying that when $|E_n - E_m| \ll \delta E$, the typical magnitude of the off-diagonal elements is

$$\langle|N_{nm}|^2\rangle \sim \frac{1}{\rho\delta E}. \tag{2.13}$$

The off-diagonal elements of the normalization matrix are therefore small provided δE is large compared to the mean level spacing. The normalization matrix $\tilde{N} = \{N_{nm}\}$ can therefore be written $\tilde{N} = \tilde{I} + \delta\tilde{N}$, where $\tilde{I}$ is the identity matrix, and where the elements of $\delta\tilde{N}$ are all small. A set of orthonormal states $|\chi_n\rangle$ can be obtained from the states $|\xi_n\rangle$ by means of a matrix with elements W_{nm}:

$$|\chi_n\rangle = \sum_m W_{nm}|\xi_m\rangle. \tag{2.14}$$

The matrix $\tilde{W} = \{W_{nm}\}$ and the matrix $\tilde{N}$ are related by $\tilde{I} = \tilde{W}^*\tilde{N}\tilde{W}^{\mathrm{T}}$, where $\tilde{I}$ is the identity matrix. This relation is solved by setting

$$\tilde{W} = (\tilde{N}^*)^{-1/2} \approx \tilde{I} - \tfrac{1}{2}\delta\tilde{N}^*. \tag{2.15}$$

3. Hamiltonian in the energy-shell basis

3.1. An approximation for the matrix elements

The time-dependent Schrödinger equation can be represented in the form (1.4), with matrix elements given by (1.5). Using (2.14) to express $|\chi_n(X)\rangle$ in terms of the energy-shell basis states $|\xi_n(X)\rangle$

$$\mathcal{H}_{nm}(t) = \sum_j\sum_{j'} W^*_{nj}W_{mj'}\langle\xi_j|\hat{H}|\xi_{j'}\rangle - \hbar\dot{\theta}_n W^*_{nj}W_{nj'}\langle\xi_j|\xi_{j'}\rangle\delta_{nm} - \mathrm{i}\hbar\dot{X}W^*_{nj}\langle\xi_j|\partial_X\big(W_{mj'}|\xi_{j'}\rangle\big). \tag{3.1}$$

Using (2.15), and neglecting all except these leading order terms in $\delta\tilde{N}$, the matrix elements (3.1) are

$$\mathcal{H}_{nm}(t) = \langle\xi_n|\hat{H}|\xi_m\rangle - \hbar\dot{\theta}_n\delta_{nm} + \tfrac{1}{2}\mathrm{i}\hbar\dot{X}[\langle\partial_X\xi_n|\xi_m\rangle - \langle\xi_n|\partial_X\xi_m\rangle]. \tag{3.2}$$

Note that this approximation is of the form (1.6), with the term proportional to $\dot{X}$ having the correct symmetry, $\mathcal{Z}^*_{mn} = -\mathcal{Z}_{nm}$. The phase θ_n is chosen to be given by integrating

$$\hbar\dot{\theta}_n = \langle\xi_n|\hat{H}|\xi_n\rangle \tag{3.3}$$

so that the diagonal elements $\mathcal{H}_{nn}$ vanish. The approximate formula (3.2) is valid in the limit $\rho\delta E \gg 1$, where the elements of $\delta\tilde{N}$ are small.

Note that the coefficients $\mathcal{H}_{nm}(t)$ are the sum of two terms, one of which is proportional to $\dot{X}$, the other independent of the rate of change of the parameter $X(t)$. It is useful to estimate the size of both of these terms, so that the smaller contribution may be neglected.

3.2. Estimate of the velocity-independent contribution

Consider how to estimate the matrix elements of the Hamiltonian, $\langle\xi_n|\hat{H}|\xi_m\rangle$ for $n \neq m$. These may be written

$$\langle\xi_n|\hat{H}|\xi_m\rangle = \sum_j\langle\xi_n|\phi_j\rangle E_j\langle\phi_j|\xi_m\rangle \equiv \sum_j X_j E_j \tag{3.4}$$

where the final equality defines the X_j, which will be modelled as uncorrelated random numbers. Approximate orthogonality of $|\xi_n\rangle$ and $|\xi_m\rangle$ implies that

$$\sum_j X_j \approx \delta_{nm}. \tag{3.5}$$

When $n \neq m$ the number of X_j that differ significantly from zero is $\sim\rho\delta E$ when $|E_n - E_m| < \delta E$, and is zero when $|E_n - E_m| \gg \delta E$.

Now consider the magnitude of $H_{nm} = \langle\xi_n|\hat{H}|\xi_m\rangle$ when E_n and E_m are close ($|E_n - E_m| < \delta E$) but not equal. This can be estimated by calculating the variance

$$\langle|H_{nm}|^2\rangle = \sum_j E_j^2\langle X_j^2\rangle + \sum_j \sum_{j'\neq j} E_j E_{j'}\langle X_j X_{j'}\rangle. \tag{3.6}$$

When $j \neq j'$, the terms $\langle X_j X_{j'}\rangle$ are expected to be very small, but neglecting the second term in (3.6) gives an unsatisfactory answer, in that the variance of the off-diagonal elements of $\hat{H}+\lambda\hat{I}$ is predicted to depend upon the arbitrary constant λ. Despite the fact that the correlations are all individually small, the sum rule (3.5) implies that the correlation coefficients $\langle X_j X_{j'}\rangle$ are themselves correlated: they must satisfy

$$\sum_j \langle X_j^2\rangle + \sum_j \sum_{j'\neq j}\langle X_j X_{j'}\rangle \approx 0. \tag{3.7}$$

Now write $E_j = \bar{E} + \delta E_j$, where

$$\bar{E} = \frac{\sum_j E_j\langle X_j^2\rangle}{\sum_j \langle X_j^2\rangle}. \tag{3.8}$$

Then (3.6) gives

$$\begin{aligned}\langle|H_{nm}|^2\rangle &= \sum_j \langle X_j^2\rangle\left(\bar{E}^2 + 2\delta E_j\bar{E} + \delta E_j^2\right) \\ &\quad + \sum_j\sum_{j'\neq j}\langle X_j X_{j'}\rangle\left(\bar{E}^2 + (\delta E_j + \delta E_{j'})\bar{E} + \delta E_j\delta E_{j'}\right) \\ &= \sum_j\sum_{j'\neq j}\langle X_j X_{j'}\rangle\left(\bar{E}(\delta E_j + \delta E_{j'}) + \delta E_j\delta E_{j'}\right) + \sum_j\langle X_j^2\rangle\delta E_j^2 \\ &\approx \sum_j \langle X_j^2\rangle\delta E_j^2. \end{aligned} \tag{3.9}$$

The simplification of this expression used (3.7) and (3.8) to eliminate terms proportional to both $\bar{E}$ and $\bar{E}^2$, and in the remaining term the correlations $\langle X_j X_{j'}\rangle$ are taken to be negligible when $j \neq j'$. The variance of the matrix elements is therefore

$$\langle|H_{nm}|^2\rangle \approx \rho p^2(0)\int_{-\infty}^{\infty} \mathrm{d}E\ (E-\bar{E})^2 f^2(E + \bar{E}_n - \bar{E}_m) f^2(E) \tag{3.10}$$

where

$$\bar{E} = \rho p^2(0)\int_{-\infty}^{\infty}\mathrm{d}E\ E f^2(E + \bar{E}_n - \bar{E}_m) f^2(E). \tag{3.11}$$

Using (2.11), this gives the estimate

$$\langle|H_{nm}|^2\rangle \sim \frac{\delta E}{\rho} \tag{3.12}$$

which is applicable for off-diagonal elements with $|E_n - E_m|$ comparable to δE.

3.3. Estimate of the velocity-dependent contribution

Now consider the contributions to the matrix elements which are proportional to $\dot{X}$. The following notations will be used

$$\begin{aligned}&\alpha_{nj} = \langle\alpha_n|\phi_j\rangle \qquad (f_n)_j = f(E_j - \bar{E}_n)\\ &(\partial_X f_n)_{jk} = \langle\phi_j|\partial_X f\big(\hat{H}(X) - \bar{E}_n(X)\big)|\phi_k\rangle.\end{aligned} \tag{3.13}$$

The coefficients determining the velocity-dependent part of the Hamiltonian are then

$$\begin{aligned}\mathcal{Z}_{nm} &= \tfrac{1}{2}\big[\langle\partial_X\xi_n|\xi_m\rangle - \langle\xi_n|\partial_X\xi_m\rangle\big]\\ &= \tfrac{1}{2}\sum_j\sum_k \alpha_{nj}\alpha^*_{mk}\big[(\partial_X f_n)_{jk}(f_m)_k - (f_n)_j(\partial_X f_m)_{jk}\big].\end{aligned} \tag{3.14}$$

Now calculate the coefficients $(\partial_X f_n)_{jk}$:

$$\begin{aligned}(\partial_X f_n)_{jk} &= \sum_l \langle\phi_j|\bigg[|\partial_X\phi_l\rangle f(E_l - \bar{E}_n)\langle\phi_l| + |\phi_l\rangle\frac{\partial f}{\partial E}(E_l - \bar{E}_n)\left(\frac{\mathrm{d}E_l}{\mathrm{d}X} - \frac{\mathrm{d}\bar{E}_n}{\mathrm{d}X}\right)\langle\phi_l|\\ &\qquad + |\phi_l\rangle f(E_l - \bar{E}_n)\langle\partial_X\phi_l|\bigg]|\phi_k\rangle\\ &= \langle\phi_j|\partial_X\phi_k\rangle(f_n)_k + (f_n)_j\langle\partial_X\phi_j|\phi_k\rangle + \left(\frac{\partial f}{\partial E}\right)_{E_j - \bar{E}_n}\left[\frac{\mathrm{d}E_j}{\mathrm{d}X} - \frac{\mathrm{d}\bar{E}_n}{\mathrm{d}X}\right]\delta_{jk}.\end{aligned} \tag{3.15}$$

Using perturbation theory

$$\langle\phi_j|\partial_X\phi_k\rangle = \frac{(\partial_X H)_{jk}}{E_k - E_j}. \tag{3.16}$$

It follows that

$$(\partial_X f_n)_{jk} = \frac{(\partial_X H)_{jk}(f_n)_k - (\partial_X H)^*_{kj}(f_n)_j}{E_k - E_j} + (\partial_E f_n)_j(\partial_X E_j - \partial_X\bar{E}_n)\delta_{jk} \tag{3.17}$$

where $(\partial_E f_n)_j = \frac{\partial f}{\partial E}(E_j - \bar{E}_n)$ and $\partial_X E_j = \mathrm{d}E_j/\mathrm{d}X$. The matrix element $\mathcal{Z}_{nm}$ can now be obtained by substituting (3.17) into (3.14). The general expression is unwieldy. Subsequent expressions will refer to the case where the wavefunctions are real-valued, so that the coefficients α_{nj} and $(\partial_X H)_{jk}$ are real. In this case

$$\begin{aligned}\mathcal{Z}_{nm} = \sum_j\sum_k \alpha_{nj}\alpha_{mk}\frac{(\partial_X H)_{jk}}{E_j - E_k}&\left[(f_n)_j(f_m)_k - \frac{1}{2}(f_n)_j(f_m)_j - \frac{1}{2}(f_n)_k(f_m)_k\right]\\ &+ \sum_j \alpha_{nj}\alpha_{mj}\big[(\partial_E f_n)_j(\partial_X E_j - \partial_X\bar{E}_n)(f_m)_j\\ &-(\partial_E f_m)_j(\partial_X E_j - \partial_X\bar{E}_m)(f_n)_j\big].\end{aligned} \tag{3.18}$$

Now estimate the variance of theses matrix elements, in terms of the variance σ^2 of matrix elements of $\partial\hat{H}/\partial X$, which is defined by (1.12). The second term in (3.18), involving only a single summation, will be assumed to make a negligible contribution to the variance and will be ignored. Assuming that the mean value of the terms in the double sum in (3.18) is zero, and that the coefficients α_{nj} and $\alpha_{nj'}$ are independent unless $j = j'$, the variance of the $\mathcal{Z}_{nm}$ is

$$\begin{aligned}\langle|\mathcal{Z}_{nm}|^2\rangle \approx \frac{1}{4}\rho^2 p^2(0)\int_{-\infty}^{\infty}\mathrm{d}E\int_{-\infty}^{\infty}\mathrm{d}E'\,\frac{\sigma^2(E-E')}{(E-E')^2}&\big[2f(E-\bar{E}_n)f(E'-\bar{E}_m)\\ &-f(E-\bar{E}_n)f(E-\bar{E}_m) - f(E'-\bar{E}_n)f(E'-\bar{E}_m)\big]^2.\end{aligned} \tag{3.19}$$

The variance has a very simple form when $|\bar{E}_n - \bar{E}_m| \gg \delta E$, and $\Delta E_c \gg \delta E$. The first of these inequalities implies that only the term containing the factor $f(E - \bar{E}_n) f(E' - \bar{E}_m)$ is significant. The second implies that the factors of f^2 can be treated as Dirac delta functions, with significant contributions only where $E \approx \bar{E}_n$ and $E' \approx \bar{E}_m$. Using the normalization properties contained in (2.10) and (2.11):

$$\begin{aligned}\langle |Z_{nm}|^2 \rangle &\approx \rho^2 p^2(0) \int_{-\infty}^{\infty} \mathrm{d}E \int_{-\infty}^{\infty} \mathrm{d}E' \, \frac{\sigma^2(E - E')}{(E - E')^2} f^2(E - \bar{E}_n) f^2(E' - \bar{E}_m) \\ &\approx \frac{\sigma^2(\bar{E}_n - \bar{E}_m)}{(\bar{E}_n - \bar{E}_m)^2}. \end{aligned} \tag{3.20}$$

When $|E_n - E_m|$ is comparable to δE, (3.19) shows that $\langle |\mathcal{Z}_{nm}|^2 \rangle \sim \sigma_0^2 / \delta E^2$.

3.4. Interpretation of the equation of motion

Having estimated the two contributions to the matrix elements, it is useful to consider the circumstances under which different terms dominate. It is also desirable to consider the extent to which the dynamics is reversible.

Using (3.11) and (3.20), the ratio of the velocity-dependent and velocity-independent coefficients of the Hamiltonian is

$$\mu \equiv \left| \frac{\hbar \mathcal{Z}_{nm}}{H_{nm}} \dot{X} \right| \sim \frac{\hbar \sigma_0 |\dot{X}|}{\delta E} \sqrt{\frac{\rho}{\delta E}}. \tag{3.21}$$

The final approximation uses the magnitudes of the largest matrix elements $\mathcal{Z}_{nm}$ and H_{nm}. The energy-shell basis set is most appropriate when the velocity-dependent contributions to the Hamiltonian are dominant. This is because the velocity-dependent terms represent the response to the time-dependent perturbation, whereas the velocity-independent terms arise because the basis states are not eigenstates of the instantaneous Hamiltonian. The condition for the velocity-dependent terms to be dominant, $\mu \gg 1$, is most easily realized when δE is small.

It is also necessary to consider whether the evolution predicted by (1.4) is reversible. The relevant question is whether reversing the path of $X(t)$, whilst continuing to increase t, reverses the evolution of the coefficients $a_n(t)$ and recovers the original state. In [2] it was shown that the evolution operator $\hat{U}_r$ for the reversed path in parameter space is the transpose of that for the original evolution. When the matrix elements of $\hat{U}$ are well approximated by real numbers, the matrix representing $\hat{U}$ is approximately orthogonal, so that $\hat{U}^T \approx \hat{U}^{-1}$. In this case the motion is reversible. When the matrix elements are complex, $\hat{U}^T$ typically does not approximate the inverse of $\hat{U}$, and the evolution is therefore not reversible.

Note that if the states χ_n are described by real wavefunctions, then the coefficients $\mathcal{Z}_{nm}$ are real numbers. The matrix elements of the evolution operator are however complex, because of the phase factors appearing in (1.4). If these phase factors were absent, the evolution would be reversible. If the phase factors do not change significantly over the characteriztic timescale τ_q over which the $a_n(t)$ fluctuate, then the evolution is not expected to be entirely irreversible. Phase factors which are multiplied by negligibly small coefficients $\mathcal{Z}_{nm}$ can be ignored. The largest significant phase factors arise when $|\bar{E}_n - \bar{E}_m| \sim \Delta E_c$, where ΔE_c is the support of $\sigma^2(\Delta E)$. The criterion for the evolution to be irreversible is therefore expressed in the form

$$\Delta E_c \tau_q / \hbar \gg 1. \tag{3.22}$$

The discussion of the solution of the time-dependent Schrödinger equation in sections 5 and 6 will focus on the case where $\mu \gg 1$ and where (3.22) is satisfied.

It is instructive to consider the expansion of a fixed state $|\psi\rangle$ in the basis formed by the states $|\chi_n(X)\rangle$:

$$|\psi\rangle = \sum_n c_n(t)|\chi_n(X)\rangle. \tag{3.23}$$

The equation of motion for the coefficients $c_n(t)$ is readily seen to be

$$\dot{c}_n = -\dot{X}\sum_m \langle\chi_n|\partial_X\chi_m\rangle c_m = \dot{X}\sum_m \mathcal{Z}_{nm}c_m. \tag{3.24}$$

This equation of motion is the same as the Schrödinger equation in the form (1.4), with both the velocity-independent terms and the phase factors removed. In cases where the velocity-independent terms are negligible, the effect of eliminating the phase factors from (1.4) is to give the equation of motion of the expansion coefficients of a fixed basis state, represented as a combination of parameter-dependent basis states. This evolution clearly is completely reversible, and has no physical significance. When (3.22) is not satisfied, it is therefore very difficult to extract information about irreversible energy diffusion from (1.4).

4. Correlation functions of basis states

4.1. Some general considerations

In order to characterize the parameter dependence of the matrix elements $\mathcal{Z}_{nm}(t)$, their correlation function will be calculated. The calculation of the correlation function is difficult, and an exact result has not been obtained in the general case. It will be convenient to discuss, in the first instance, the correlation function of various simpler objects.

The first of these simpler matrix elements is

$$\begin{aligned}\mathcal{A}_{nm} &= \langle\alpha_n|f(\hat{H})|\alpha_m\rangle \\ &= \sum_j \langle\alpha_n|\phi_j\rangle f(E_j)\langle\phi_j|\alpha_m\rangle = \sum_j \alpha_{nj}f_j\alpha^*_{mj}\end{aligned} \tag{4.1}$$

where a condensed notation similar to (3.12) has been used. It will be assumed that the coefficients α_{nj} are real, and that they are uncorrelated, satisfying

$$\begin{aligned}&\langle\alpha_{nj}\alpha_{mj}\rangle = \delta_{nm}\,p(E_j - \bar{E}_n) \\ &\langle\alpha_{nj}\alpha_{mj}\alpha_{n'j'}\alpha_{m'j'}\rangle = \langle\alpha_{nj}\alpha_{mj}\rangle\langle\alpha_{n'j'}\alpha_{m'j'}\rangle + \langle\alpha_{nj}\alpha_{n'j'}\rangle\langle\alpha_{mj}\alpha_{m'j'}\rangle + \langle\alpha_{nj}\alpha_{m'j'}\rangle\langle\alpha_{mj}\alpha_{n'j'}\rangle.\end{aligned} \tag{4.2}$$

The matrix elements $\mathcal{A}_{nm}$ and $\mathcal{A}_{n'm'}$ are therefore uncorrelated (unless $n = n'$ and $m = m'$, or $n = m'$ and $m = n'$). If the same assumption (4.2) is applied to the matrix elements $\mathcal{Z}_{nm}$, these too are predicted to be uncorrelated, so that

$$\langle\mathcal{Z}_{nm}(X + X_0)\mathcal{Z}_{n'm'}(X_0)\rangle = (\delta_{nn'}\delta_{mm'} - \delta_{nm'}\delta_{mn'})C(X, \bar{E}_n - \bar{E}_m). \tag{4.3}$$

The correlation properties of these matrix elements are therefore described by a single function, $C(X, \Delta E)$.

The following quantity will prove crucial to calculating these correlation functions:

$$P_{nm}(X) = \langle|\langle\phi_m(X_0 + X)|\phi_n(X_0)\rangle|^2\rangle \tag{4.4}$$

where the angle brackets represent an average over states. In [7] an argument was proposed for the form of $P_{nm}(X)$, which was derived for a random matrix model, but which is expected to be quite generally applicable. The form predicted is $P_{nm}(X) = P(X, \bar{E}_n - \bar{E}_m)$, where

$$P(X, \Delta E) = \frac{\sigma_0^2 X^2}{\Delta E^2 + (\pi\rho\sigma_0^2 X^2)^2} \tag{4.5}$$

and where $\sigma_0^2 = \sigma^2(0)$. This expression is expected to hold when considering complex quantum systems without symmetries or constants of motion, when $\Delta E \ll \Delta E_c$. This formula will now be used to calculate the correlation function of matrix elements such as (4.1).

4.2. Models for matrix element correlations

It will be instructive to consider the correlation functions of three different types of matrix elements in turn. First consider the correlation function for elements of the form (4.1). The correlation coefficient is independent of the indices n and m, and it is sufficient to calculate the correlation function $C_{\mathcal{A}}(X)$ of an object $\mathcal{A}(X)$, defined as follows:

$$\begin{aligned}\mathcal{A}(X) &= \langle\alpha|f\big(\hat{H}(X)\big)|\beta\rangle \\ C_{\mathcal{A}}(X) &= \langle\mathcal{A}(X_0+X)\mathcal{A}(X_0)\rangle.\end{aligned} \tag{4.6}$$

Using the notation $\alpha_n = \langle\alpha|\phi_n(0)\rangle$, $\beta_n = \langle\phi_n(0)|\beta\rangle$:

$$C_{\mathcal{A}}(X) = \left\langle \sum_n \alpha_n f(E_n(0))\beta_n \sum_{n'} \alpha_{n'} \sum_m \langle\phi_{n'}(0)|\phi_m(X)\rangle f(E_m(X))\langle\phi_m(X)|\phi_{n'}(0)\rangle\beta_{n'}\right\rangle. \tag{4.7}$$

This expression will be simplified using the assumption that α_n and β_n are uncorrelated, i.e. $\langle\alpha_n\alpha_{n'}\rangle = \langle\alpha_n^2\rangle\delta_{nn'}$, $\langle\alpha_n\beta_{n'}\rangle = 0$, and $\langle\beta_n\beta_{n'}\rangle = \langle\beta_n^2\rangle\delta_{nn'}$. Writing $f_n = f(E_n(0))$, $f_n' = f(E_n(X))$, the correlation function (4.7) is then given by

$$C_{\mathcal{A}}(X) = \sum_n \sum_m \langle\alpha_n^2\rangle\,\langle\beta_n^2\rangle\, f_n\, f_m'\, P_{nm}(X). \tag{4.8}$$

Now assume that $\langle\alpha_n^2\rangle = \langle\beta_n^2\rangle$ and that these are independent of n for all energies for which the f_n are significant (this is equivalent to the assumption $\delta E \ll \Delta E$ discussed in section 2). The correlation function is then

$$C_{\mathcal{A}}(X) = \langle\alpha^2\rangle^2\rho^2 \int_{-\infty}^{\infty} \mathrm{d}E \int_{-\infty}^{\infty} \mathrm{d}E'\; f(E)f(E')P(X,\Delta E). \tag{4.9}$$

Writing $f(E) = F(E/\delta E)$, this correlation function may be expressed in the form

$$C_{\mathcal{A}}(X) = \langle\alpha^2\rangle^2\,\rho\,\delta E\,\Phi(\zeta) \qquad \zeta = \frac{\pi\rho\sigma_0^2X^2}{\delta E} \tag{4.10}$$

where

$$\Phi(\zeta) = \frac{1}{\pi}\int_{-\infty}^{\infty}\mathrm{d}x \int_{-\infty}^{\infty}\mathrm{d}x'\; F(x)F(x')\frac{\zeta}{(x-x')^2+\zeta^2}. \tag{4.11}$$

Where the function F is Gaussian, $F(x) = \exp(-x^2/2)$

$$\Phi(\zeta) = \sqrt{\pi}\exp(\zeta^2/4)\mathrm{erfc}(\zeta/2). \tag{4.12}$$

The scale length $\delta X_{\delta E}$ and the timescale τ_{q} for the decay of matrix element correlations are therefore

$$\delta X_{\delta E} = \frac{1}{\sigma_0}\sqrt{\frac{\delta E}{\rho}} \qquad \tau_{\mathrm{q}} = \frac{1}{\sigma_0|\dot{X}|}\sqrt{\frac{\delta E}{\rho}}. \tag{4.13}$$

Equations (3.14) and (2.5) show that the matrix elements $\mathcal{Z}_{nm}$ contain derivatives of the form $\partial_X f(\hat{H}-E)$. Accordingly, it will be instructive to consider the correlation function of the matrix element

$$\mathcal{B}(X) \equiv \langle\alpha|\partial_X f\big(\hat{H}(X)\big)|\beta\rangle = \partial_X\mathcal{A}(X). \tag{4.14}$$

This correlation function $C_{\mathcal{B}}(X)$ is

$$\begin{aligned}C_{\mathcal{B}}(X) &= \langle\mathcal{B}(X_0+X)\mathcal{B}(X_0)\rangle = \frac{\partial^2}{\partial X_1\partial X_2}\big\langle\mathcal{A}(X_1)\mathcal{A}(X_2)\big\rangle\big|_{X_1=X,X_2=0} \\ &= \frac{\partial^2}{\partial X_1\partial X_2}C_{\mathcal{A}}(X_1-X_2)\big|_{X_1=X,X_2=0}.\end{aligned} \tag{4.15}$$

It follows that

$$C_{\mathcal{B}}(X) = -\frac{\partial^2 C_{\mathcal{A}}(X)}{\partial^2 X} = -2\pi\rho^2\sigma_0^2\langle\alpha^2\rangle^2\left[2\zeta\frac{\mathrm{d}^2\Phi(\zeta)}{\mathrm{d}\zeta^2} + \frac{\mathrm{d}\Phi(\zeta)}{\mathrm{d}\zeta}\right] \tag{4.16}$$

where the final equality has used (4.10). The matrix elements $\mathcal{B}(X)$ therefore have the same characteriztic correlation length as the $\mathcal{A}(X)$, namely that given by (4.13).

Next, consider the correlation function of the matrix element

$$\mathcal{C}(X) = \langle\alpha|g(\hat{H}(X))\partial_X f(\hat{H}(X))|\beta\rangle = \langle A(X)|B(X)\rangle \tag{4.17}$$

where $|A(X)\rangle = g(\hat{H})|\alpha\rangle$, and $|B(X)\rangle = \partial_X f(\hat{H})|\beta\rangle$. This matrix element is similar in structure to (3.14). I did not find a general formula for the correlation function of these matrix elements. In the case where the support of the functions f and g do not overlap, it is possible to estimate the correlation function. In this case, the states $|A(X)\rangle$ and $|B(X)\rangle$ may be assumed to be statistically independent. The correlation function is therefore proportional to the product of correlation functions characterizing these states. To make this more concrete, assume that $\{|\gamma_n\rangle\}$ are a complete set of states. The states $|A(X)\rangle$ and $|B(X)\rangle$ are assumed to be drawn from ensembles having the following correlation properties:

$$\begin{aligned}
&\langle\!\langle A(X_0+X)|\gamma_n\rangle\langle\gamma_{n'}|A(X_0)\rangle\!\rangle = a_n\delta_{nn'}C_{AA}(X)\\
&\langle\!\langle B(X_0+X)|\gamma_n\rangle\langle\gamma_{n'}|B(X_0)\rangle\!\rangle = b_n\delta_{nn'}C_{BB}(X)\\
&\langle\!\langle A(X_0+X)|\gamma_n\rangle\langle\gamma_{n'}|B(X_0)\rangle\!\rangle = 0
\end{aligned} \tag{4.18}$$

where the averages are over X_0, the weights a_n and b_n are non-negative real numbers, and the correlation functions $C_{AA}(X)$ and $C_{BB}(X)$ are independent of the index n. The required correlation function $C_{\mathcal{C}}(X)$ can then be written in terms of the correlation functions defined in (4.18), i.e.

$$\begin{aligned}
C_{\mathcal{C}}(X) &\equiv \langle\!\langle A(X_0+X)|B(X_0+X)\rangle\langle A(X_0)|B(X_0)\rangle\!\rangle\\
&= \sum_n\sum_{n'}\langle\!\langle A(X_0+X)|\gamma_n\rangle\langle\gamma_n|B(X_0+X)\rangle\!\rangle\langle\!\langle A(X_0)|\gamma_{n'}\rangle\langle\gamma_{n'}|B(X_0)\rangle\!\rangle\\
&\approx C_{AA}(X)C_{BB}(X)\sum_n a_n b_n = K\,C_{AA}(X)C_{BB}(X)
\end{aligned} \tag{4.19}$$

where K is a constant.

Finally, consider the correlation function of the matrix elements (3.14). These matrix elements are of the form

$$\mathcal{Z}(X) = \tfrac{1}{2}\langle\alpha|\partial_X f(\hat{H})g(\hat{H}) - f(\hat{H})\partial_X g(\hat{H})|\beta\rangle = \tfrac{1}{2}\big[\langle A_X|B_X\rangle - \langle C_X|D_X\rangle\big]. \tag{4.20}$$

where $|A_X\rangle = \partial_X\hat{f}_X|\alpha\rangle$, $|B_X\rangle = \hat{g}_X|\beta\rangle$, $|C_X\rangle = \hat{f}_X|\alpha\rangle$, and $|D_X\rangle = \partial_X\hat{g}_X|\beta\rangle$, with $\hat{f}_X = f(\hat{H}(X))$, $\hat{g}_X = g(\hat{H}(X))$. The correlation function of this matrix element is

$$\begin{aligned}
C_{\mathcal{Z}}(X) &= \langle\mathcal{Z}(X_0+X)\mathcal{Z}(X_0)\rangle\\
&= \tfrac{1}{4}\big[\langle\!\langle A_X|B_X\rangle\langle A_0|B_0\rangle\!\rangle + \langle\!\langle C_X|D_X\rangle\langle C_0|D_0\rangle\!\rangle\\
&\quad -\langle\!\langle A_X|B_X\rangle\langle C_0|D_0\rangle\!\rangle - \langle\!\langle C_X|D_X\rangle\langle A_0|B_0\rangle\!\rangle\big]\\
&= \tfrac{1}{2}\big[C_1(X) - C_2(X)\big].
\end{aligned} \tag{4.21}$$

The final equality in (4.21) uses the fact that the first pair of correlations between pairs of Dirac brackets are equal (and are denoted $C_1(X)$), as are the second pair (denoted $C_2(X)$). I will treat the functional forms of the correlation functions $C_1(X)$ and $C_2(X)$ in due course. First consider their values at $X = 0$. Using the approach of section 3.3, and setting $f(E) \to f(E - \bar{E}_n)$,

$g(E) \to f(E-\bar{E}_m)$, $\langle\alpha^2\rangle = \langle\beta^2\rangle = p(0)$ in order give agreement with the notation used there, i.e.

$$C_1(0) = \frac{1}{2}\rho^2 p^2(0)\int_{-\infty}^{\infty}\mathrm{d}E\int_{-\infty}^{\infty}\mathrm{d}E'\,\frac{\sigma^2(E-E')}{(E-E')^2}$$
$$\times\Big[\big(f(E-\bar{E}_n)-f(E'-\bar{E}_n)\big)^2 f^2(E'-\bar{E}_m)+\big(f(E-\bar{E}_m)-f(E'-\bar{E}_m)\big)^2 f^2(E-\bar{E}_n)\Big]$$
$$C_2(0) = \rho^2 p^2(0)\int_{-\infty}^{\infty}\mathrm{d}E\int_{-\infty}^{\infty}\mathrm{d}E'\,\frac{\sigma^2(E-E')}{(E-E')^2}$$
$$\times\Big[\big(f(E-\bar{E}_n)-f(E'-\bar{E}_n)\big)\big(f(E-\bar{E}_m)-f(E'-\bar{E}_m)\big)f(E-\bar{E}_m)f(E'-\bar{E}_n)\Big]. \tag{4.22}$$

Note that when $|\bar{E}_n-\bar{E}_m| \gg \delta E$

$$C_1(0) \approx -C_2(0) \approx \frac{\sigma^2(\bar{E}_n-\bar{E}_m)}{(\bar{E}_n-\bar{E}_m)^2}. \tag{4.23}$$

Now the form of the correlation function $C_1(X)$ has already been obtained in (4.19):

$$C_1(X) = K_1\,\Phi(\zeta)\left[\frac{\mathrm{d}\Phi(\zeta)}{\mathrm{d}\zeta}+2\zeta\frac{\mathrm{d}^2\Phi(\zeta)}{\mathrm{d}\zeta^2}\right] \tag{4.24}$$

where K_1 is a constant. To determine the form of the correlation function $C_2(X)$, note that $\partial_X(\hat{f}_X\hat{g}_X) = \hat{f}_X(\partial_X\hat{g}_X)+(\partial_X\hat{f}_X)\hat{g}_X$, and introduce a correlation function

$$C_3(X) = \big\langle\langle\alpha|\partial_X(\hat{f}_X\hat{g}_X)|\beta\rangle\langle\alpha|\partial_X(\hat{f}_0\hat{g}_0)|\beta\rangle\big\rangle. \tag{4.25}$$

Note that

$$C_3(X) = 2\big[C_1(X)+C_2(X)\big] \tag{4.26}$$

and also that $C_3(X)$ is a correlation function of the same form as $C_{\mathcal{B}}(X)$, with $\hat{f}_X$ replaced by the product $\hat{f}_X\hat{g}_X$. This correlation function may therefore be calculated using (4.16), and the function $C_2(X)$ is obtained using (4.26) and (4.24). In the case where we wish to obtain the correlation functions of matrix elements with $|\bar{E}_n-\bar{E}_m| \gg \delta E$, the functions $f(E)$ and $g(E)$ are replaced by functions $f(E-\bar{E}_n)$ and $g(E-\bar{E}_m)$, which have non-overlapping support. The product $f(E)g(E)$ is therefore negligible in this case, so that $C_3(X) \approx 0$, implying that $C_2(X) \approx -C_1(X)$ in that case. For the particular choice of $f(E)$ given by (2.1), equations (4.12), (4.23) and (4.24) give

$$C_{\mathcal{Z}}(X) = \langle\mathcal{Z}_{nm}(X)\mathcal{Z}_{n'm'}(0)\rangle \approx (\delta_{nn'}\delta_{mm'}-\delta_{nm'}\delta_{n'm})\frac{\sigma^2(\bar{E}_n-\bar{E}_m)}{(\bar{E}_n-\bar{E}_m)^2}\Psi(\zeta) \tag{4.27}$$

where

$$\Psi(\zeta) = \exp(\zeta^2/4)\mathrm{erfc}(\zeta/2)\big[(\zeta^2+1)-\tfrac{1}{2}\sqrt{\pi}\zeta(\zeta^2+3)\exp(\zeta^2/4)\mathrm{erfc}(\zeta/2)\big] \tag{4.28}$$

(where ζ is defined in (4.10)). Equation (4.27) is valid when $\delta E \ll |E_n-E_m| \ll \Delta E_{\mathrm{c}}$.

5. Energy diffusion

Now consider the use of the energy-shell basis states to characterize solutions of the time-dependent Schrödinger equation. These states could be used for a numerical solution of the exact Schrödinger equation. It is, however, instructive to discuss a model Schrödinger equation with random matrix elements, chosen to have the same statistical properties as the matrix elements in the energy-shell basis. It will be assumed that $|\dot{X}|$ is sufficiently large that the velocity-independent term in the equation of motion (1.4) can be neglected (the condition

for this was discussed in section 3.4). The Schrödinger equation (1.4) is therefore modelled by a system of stochastic differential equations for expansion coefficients $a_n(t)$. This will be written in the form

$$\dot{a}_n = \dot{X} \sum_m \mathcal{Z}_{nm}(\dot{X}t) \exp\left[\mathrm{i}\big(\bar{E}_n - \bar{E}_m\big)t/\hbar\right] a_m \tag{5.1}$$

with $\mathcal{Z}_{nn} = 0$, $\mathcal{Z}_{nm}(t) = -\mathcal{Z}^*_{mn}(t)$ modelled as random functions. Rather than solving (3.3), the phase factor in (5.1) has been simplified by using the approximate energies $\bar{E}_n$ and assuming that their X dependence may be neglected. This approximation is not expected to have a significant influence on any of the results discussed below.

The $\mathcal{Z}_{nm}$ are the smoothly varying real-valued random functions satisfying

$$\begin{aligned} &\langle \mathcal{Z}_{nm}(t)\rangle = 0 \\ &\langle \mathcal{Z}_{nm}(t)\mathcal{Z}_{n'm'}(t')\rangle = (\delta_{nn'}\delta_{mm'} - \delta_{nm'}\delta_{n'm})W(\bar{E}_n - \bar{E}_m)c(t-t'). \end{aligned} \tag{5.2}$$

The correlation function in (5.2) will be taken to be that obtained in (4.27): $c(t) = \Psi(\zeta)$, with $\zeta = \pi\rho\sigma^2\dot{X}^2t^2/\delta E$. The approach of replacing the exact Schrödinger equation by a system of stochastic differential equations was used in [2] for the case where the matrix elements $\mathcal{Z}_{nm}$ were taken to be those obtained using the adiabatic basis. Most of the discussion below follows sections 4 and 5 of [2]. The remainder of this section will summarize the relevant results from that earlier paper, emphasizing the points which differ when the energy-shell basis is used instead of the adiabatic basis.

Reference [2] discussed a perturbative treatment of (5.1), which corresponds to taking the limit $\dot{X} \to 0$, holding the timescale for decay of the correlation function $c(t)$ fixed. It was shown that in the limit $\dot{X} \to 0$ the probability for occupation of the state with index n, namely $P_n = \langle |a_n|^2\rangle$, obeys the rate equation

$$\frac{\mathrm{d}P_n}{\mathrm{d}t} = \sum_m R_{nm}(P_m - P_n). \tag{5.3}$$

The rate constants are given by

$$R_{nm} = R(\Delta E) = \dot{X}^2 \int_{-\infty}^{\infty} \mathrm{d}t \ \exp(\mathrm{i}\Delta E t/\hbar)\, W(\Delta E)\, c(t) \tag{5.4}$$

with $\Delta E - \bar{E}_n - \bar{E}_m$. This description is valid provided the product λ of the total rate for transitions out of a state and the timescale τ_{q} over which correlations of matrix elements decay is a small number

$$\lambda \equiv \tau_{\mathrm{q}} \sum_m R_{nm} \ll 1. \tag{5.5}$$

Now consider how λ may be estimated. The results of section 3 indicate that the variance of the matrix elements $\mathcal{Z}_{nm}$ is approximately $\sigma^2(\Delta E)/\Delta E^2$ when $\Delta E \gg \delta E$, and approximately $\sigma_0^2/\delta E^2$ when $\Delta E \ll \delta E$. The largest rate constants are therefore of size $R_{\max} \sim \tau_{\mathrm{q}}\dot{X}^2\sigma_0^2/\delta E^2$. The number of rate constants of this magnitude is $\sim\rho\delta E$. Using (4.13), the quantity λ is therefore

$$\lambda \sim \rho\delta E R_{\max}\tau_{\mathrm{q}} \sim 1. \tag{5.6}$$

The perturbative description provided by (5.3) and (5.4) is valid when $\lambda \ll 1$, and fails when $\lambda \gg 1$. The physically significant situation is therefore the marginal case, where the perturbative expression can be assumed to be a useful approximation, but not necessarily a

precise evaluation of the diffusion constant. A similar conclusion was obtained in [2] for the special case of the adiabatic basis.

Now consider the estimation of the energy-diffusion constant, D_E, defined by (1.14) and (1.15). Again, this follows the approach of [2] quite closely. The diffusion constant is estimated as

$$D_E \approx \frac{1}{2\rho^2}\sum_m R_{nm}(n-m)^2 \approx \frac{1}{2\rho}\int_{-\infty}^{\infty} \mathrm{d}\Delta E\ R(\Delta E)\,\Delta E^2. \tag{5.7}$$

It will be assumed that the integral is dominated by contributions from the region where $\Delta E \gg \delta E$. The transition rate in this region is estimated using (4.27), which gives

$$R(\Delta E) \approx \dot{X}^2 \frac{\sigma^2(\Delta E)}{\Delta E^2}\int_{-\infty}^{\infty} \mathrm{d}\tau\ \exp(\mathrm{i}\Delta E\tau/\hbar)\,c(\tau) \tag{5.8}$$

where $c(0) = 1$, and where the support of $c(\tau)$ is τ_q. The integral can be approximated by $2\pi\hbar\delta_\nu(\Delta E)$, where $\delta_\nu(x)$ is a broadened delta function with support $\nu = \hbar/\tau_\mathrm{q}$. Inserting this approximation into (5.7) leads to the estimate

$$D_E \sim \pi\rho\hbar\sigma_0^2\dot{X}^2 \tag{5.9}$$

provided ν is smaller than support ΔE_c of the function $\sigma^2(\Delta E)$. The condition for (5.9) to be applicable is therefore that $\nu/\Delta E_\mathrm{c}$ is small, i.e.

$$\eta_{\delta E} \equiv \frac{|\dot{X}|\sigma_0\hbar}{\Delta E_\mathrm{c}}\sqrt{\frac{\rho}{\delta E}} \ll 1. \tag{5.10}$$

When (5.10) is satisfied, the estimate (5.9) for the diffusion constant is expected to be applicable. It was noted in section 1.3 that (5.9) implies a rate of dissipation which is equivalent to that predicted by the Kubo formula. A similar criterion was given in [2] for the special case where the adiabatic basis states were used, and (5.10) reduces to the inequality given in [2] when $\delta E \sim \rho^{-1}$. It should also be checked that the condition for the dynamics to be irreversible is satisfied. Using the estimate for τ_q given in (4.13), it is seen that the criterion (3.22) is equivalent to (5.10).

The conclusions of this section may be summarized as follows. Equation (5.9) was obtained as an estimate of the energy-diffusion constant. This was based upon a perturbative calculation, valid when the dimensionless coupling constant λ is small. The constant λ is in fact of order unity, so that the argument presented above is not sufficient to show that (5.9) is a precise estimate of D_E. Two conditions must be satisfied in order for the estimate (5.9) to be justified. First, the equation of motion was assumed to be dominated by the velocity-dependent term, which requires that δE is sufficiently small that (3.21) is satisfied. Secondly, the estimate (5.9) depends upon the decorrelation time τ_q being given correctly by (4.13), and consequently upon δE being made sufficiently large that (5.10) is satisfied. These two conditions can be satisfied simultaneously provided $\Delta E_\mathrm{c} \gg \delta E$. If (5.10) is not satisfied, it is not possible to make any reliable prediction about D_E from these arguments.

6. Discussion

This paper has characterized a new type of basis set, in terms of matrix elements of the Hamiltonian and their parametric correlations. The principle motivation for this work was to use the statistics of these matrix elements in a stochastic model of the Schrödinger equation, and to characterize solutions of the time-dependent Schrödinger equation by means of the energy-diffusion constant, D_E. This energy-diffusion constant is directly related to the rate of dissipation.

In the Introduction it was remarked that (1.17) gives a rate of dissipation which is in agreement with the Kubo–Greenwood formula. The derivation of the Kubo–Greenwood formula is perturbative, in that it is only strictly justified if the excursion of the parameter $X(t)$ is extremely small. The energy-diffusion constant is defined in terms of a finite excursion of $X(t)$, and there is no guarantee that the energy-diffusion constant will be given correctly by (1.17). For systems which are well described by chaotic classical dynamics, the energy-diffusion constant may be obtained in terms of a classical correlation function [8], which can be related to the matrix element statistic $\sigma^2(\Delta E)$ by a semiclassical relation [9]. In these systems (1.17) must be valid in the limit $\hbar \to 0$. In the case of systems which are not well described by chaotic classical motion, there is still no satisfactory general theory for the energy-diffusion constant D_E.

The results of this paper should be compared with [2], which used a stochastic differential equation to model the Schrödinger equation in the adiabatic basis. In that paper it was argued that D_E is given approximately by (1.17), provided that $|\dot{X}|$ is sufficiently small that a dimensionless parameter η is small compared to unity, i.e.

$$\eta \equiv \frac{\hbar \rho \sigma_0 |\dot{X}|}{\Delta E_{\rm c}} \ll 1. \tag{6.1}$$

The physical origin for this inequality is that when (6.1) is violated, the rapid fluctuations of the matrix elements could suppress transitions between states. Reference [2] presented two discordant but not incompatible arguments about the validity of the condition (6.1). Numerical experiments on a class of banded random matrix models showed that (1.17) is an accurate expression for D_E when (6.1) is satisfied, and that for these systems (6.1) does correctly predict the onset of the failure of (1.17) as $|\dot{X}|$ is increased. By contrast, it was also shown that this behaviour would lead to a breakdown of ohmic dissipation (i.e. $D_E \propto \dot{X}^2$) at unphysically small values of $|\dot{X}|$, both in systems described by classical dynamics, and in a model for dissipation in electrical conductors. It was argued that in these latter systems there are correlations between matrix elements which ensure that (6.1) does not represent a threshold for failure of the Kubo–Greenwood formula.

This paper has defined an alternative set of states, the energy-shell basis states, which fluctuate more slowly than the adiabatic states, and which therefore exhibit the correlations which were hypothesized in [2]. For these states condition (6.1) is replaced by an analogous condition (5.10), which allows larger values of $|\dot{X}|$ before the argument supporting (1.17) breaks down. This extension of the range of validity of (1.17) was achieved at the expense of an assumption, contained in (4.5), concerning the parametric dependence of eigenfunctions. In the banded random matrix model discussed in [2], (6.1) was found to be the relevant criterion for failure of (1.17), indicating that for this model there is a failure of the assumptions underlying (4.5) (which was based upon full, as opposed to banded, random matrices).

The optimal value of δE to obtain the highest possible threshold is obtained by setting $\delta E \sim \Delta E_{\rm c}$, which is at the borderline for mutual compatibility of the inequalities (3.21) and (5.10). This leads to the following estimate for the maximum value of $|\dot{X}|$ for which (1.17) is shown to be applicable:

$$|\dot{X}| \ll \dot{X}_{\rm max} \sim \frac{\Delta E_{\rm c}^{3/2}}{\rho^{1/2} \hbar \sigma_0}. \tag{6.2}$$

It should be emphasized that the inequality (6.2) does not necessarily represent a threshold for the breakdown of (1.17) in any given system. Using the estimates discussed in [2], the value of $\dot{X}_{\rm max}$ given by (6.2) is found to vanish in the limit $\hbar \to 0$, holding all classical parameters fixed. This indicates that the condition (5.10) is therefore still too restrictive to describe the behaviour of quantum systems which are well described by classical dynamics.

The velocity scale defined by (6.2) has been discussed in earlier papers by Cohen [10, 11], who proposes that it 'controls the route towards quantal-classical correspondence' and that when this velocity scale is exceeded, the rate of dissipation 'may be qualitatively different'. A comparison of the present paper with these earlier works shows that the nature of the arguments leading to (6.2) are quite distinct. He also claims that (1.17) is always valid when $|\dot{X}|$ is lower than the estimate (6.2), which contradicts the numerical results in [2].

In fact the behaviour of the energy-diffusion constant D_E appears to be highly system dependent. It has already been pointed out that neither (6.1) nor (6.2) determine the failure of (1.17) for semiclassical systems, whereas numerical evidence shows that (6.1) is the relevant criterion for a class of banded random matrix models. Another class of random matrix models has been discussed [12] in which (1.17) also fails in a certain range of parameters, and where the boundary is not determined by either (6.1) or (6.2).

The use of the energy-shell basis, as detailed in this paper, represents an advance in understanding the dynamics of complex quantum systems, but does not yet give a complete description. It has been used here to extend the range of values of $|\dot{X}|$ for which (1.17) is applicable, subject to the assumptions of a random matrix model, contained in (4.5). The approach is potentially quite general in its scope, but the discussions from section 4 onwards used (4.5), resulting from the random matrix model discussed in [7] to analyse the parametric correlations of matrix elements. It is anticipated valuable insights into the behaviour of the energy diffusion constant in different systems will be gained by dropping this assumption, and examining 'non-universal' aspects of the correlation of the matrix elements $\mathcal{Z}_{nm}(X)$.

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