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QUANTUM ELECTRONICS

Irreversible Transitions in the Wigner Representation

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Abstract. Irreversible transitions are studied in the Wigner representation. When Fermi Golden Rule (FGR) applies, the transition rate is given by the phase-space overlap integral between the initial Wigner function and the final quasi-distribution which is the Wigner transform of the microcanonical density matrix. Classical approximations and various applications are discussed.

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1. Introduction

Irreversible processes of relaxation and decay are often subject to Fermi Golden Rule (FGR). These include nuclear decay, radiationless transitions of polyatomic molecules, predissociation, photochemical processes, and some processes involving cold atoms in magnetic and optical traps, to name just a few physical systems [1–4]. As detailed below, following Refs. [5–7] we are suggesting a phase-space Wigner function approach [8–11] to the study of such FGR processes [12–18].

2. Irreversible Transitions

Many processes can be described by the Fermi Golden Rule. The transition rate of these processes is generally given by

$$\Gamma = \frac{2\pi}{\hbar}|\kappa|^2 \int_{-\infty}^{\infty} dE \ \mathrm{Tr}\left[\hat{\rho}_I(E)\hat{\rho}_F(E)\right] , \tag{1}$$

where $|\kappa|^2$ is the coupling strength and $\hat{\rho}_{I/F}$ are the initial and final density matrices, respectively. The final density matrix is the density matrix of the microcanonical

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ensemble at energy E

$$\hat{\rho}_F(E) = \sum_{\{k\}} \left|\phi_{\{k\}}\right\rangle \left\langle\phi_{\{k\}}\right| \delta\left(E_F^{\{k\}} - E\right) , \tag{2}$$

where $\phi_{\{k\}}$ are eigenstates of the final Hamiltonian $H_F(q,p)$ with eigenvalues $E_F^{\{k\}}$.

When the initial state is a pure and stationary state, the initial density matrix is given in terms of a single eigenstate $\psi_{\{j\}}$ of the initial Hamiltonian $H_I(q,p)$

$$\hat{\rho}_I^{\{j\}}(E) = \left|\psi_{\{j\}}\right\rangle \left\langle\psi_{\{j\}}\right| \delta\left(E_I^{\{j\}} + E_0 - E\right) . \tag{3}$$

Here $E_I^{\{j\}}$ is the eigenenergy of the initial state and E_0 is the energy difference between the minima of the initial and final potentials. Integration over E reproduces the well-known form:

$$\Gamma_{\mathrm{FGR}}^{\{j\}}(E_0) = \frac{2\pi}{\hbar}|\kappa|^2 \sum_{\{k\}} \left|\left\langle\phi_{\{k\}}|\psi_{\{j\}}\right\rangle\right|^2 \delta\left(E_F^{\{k\}} - E_I^{\{j\}} - E_0\right) . \tag{4}$$

3. FGR in the Wigner Representation

A quantum state which is given in general by the density matrix $\hat{\rho}$ is represented in phase space by its Weyl symbol, the Wigner function, [8–11],

$$\rho(\vec{q},\vec{p}) \equiv \frac{1}{(2\pi\hbar)^d} \int_{-\infty}^{\infty} d\vec{\eta} \left\langle \vec{q} + \frac{\vec{\eta}}{2} \right| \hat{\rho} \left| \vec{q} - \frac{\vec{\eta}}{2} \right\rangle e^{-i\vec{p}\cdot\vec{\eta}/\hbar} . \tag{5}$$

The Wigner function is a quasi-distribution; it is real but can be negative.

The FGR transition rate is given in phase space by the overlap integral,

$$\Gamma = \frac{2\pi}{\hbar}|\kappa|^2 \ (2\pi\hbar)^d \int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} d\vec{q}d\vec{p} \ \rho_F^E(\vec{q},\vec{p})\rho_I^E(\vec{q},\vec{p}) , \tag{6}$$

where $\rho_I^E(\vec{q},\vec{p})$ and $\rho_F^E(\vec{q},\vec{p})$ are the Wigner transforms of $\hat{\rho}_I(E)$ and $\hat{\rho}_F(E)$, respectively, and Eq. (6) is Eq. (1) in the Wigner representation. The Wigner representation of quantum mechanics is an exact representation with no intrinsic approximation.

The classical limit of Eq. (6) is obtained by taking the classical limit of the Wigner functions $\rho_I^E(\vec{q},\vec{p})$ and $\rho_F^E(\vec{q},\vec{p})$ in the integrand of Eq. (6). When $\rho_I^E(\vec{q},\vec{p})$ is the Wigner function of a pure state it is often better to apply the classical limit only to $\rho_F^E(\vec{q},\vec{p})$, while a thermal initial distribution justifies taking the classical limit for both the initial and final states.

The Wigner function of the microcanonical density has a well-known classical limit:

$$\rho_F^E(\vec{q},\vec{p}) \approx \frac{1}{(2\pi\hbar)^d} \delta\left(E - H_F(\vec{q},\vec{p})\right) . \tag{7}$$

For the derivation of this classical limit and its quantum corrections see Refs. [5–7].

The classical limit of FGR is obtained by substituting Eq. (7) in Eq. (6):

$$\Gamma_{\mathrm{C}}^{\{j\}}(E_0) \equiv \frac{2\pi}{\hbar}|\kappa|^2 \frac{1}{(2\pi\hbar)^d} \int_{-\infty}^{\infty} d\vec{q}d\vec{p}\ \rho_I^{\{j\}}(\vec{q},\vec{p})\ \delta\left(H_F(\vec{q},\vec{p}) - E_I^{\{j\}} - E_0\right). \quad (8)$$

Equation (8) gives the leading order in a semiclassical expansion. Higher order terms in the expansion were derived in Refs. [6, 7] for pure initial states and in Ref. [15] the expansion was developed for thermal initial distributions.

4. Application to Atom Lasers

In Ref. [15] the classical limit of FGR in the Wigner representation for thermal initial states was developed and applied to model systems of harmonic oscillators in one and three dimensions and square wells where the approximate results were successfully compared with exact quantum calculations. It was then applied there to the calculation of finite temperature effects on weak output coupling of a magnetically trapped atomic Bose gas so as to form an atom laser. In this system, the initial and final Hamiltonians correspond to the effective potentials in the magnetic trap that the atoms experience while being in different hyperfine levels. Our method was useful for this purpose because it is not restricted to Bolzman distributions. Likewise, the fact that the Hamiltonian $H_I(\vec{q},\vec{p})$ need not be of the simple form separable to a kinetic energy and a potential energy parts, allowed for a treatment of the effective Hamiltonian of the quasi-particle excitations which was given by a nonlinear function of the potential, the momentum and the density.

5. Application to Energy Transfer in Polyatomic Molecules

In Ref. [13], following Ref. [12] we suggested to study the integrand of Eq. (8) so as to recognize a point(s) or region(s) in phase space that contribute most to the integral. When such a point or region is found we suggested to interpret it as the positions and momenta of the nuclei during the electronic transition. In particular, for non-vertical, or Franck–Condon-suppressed transitions we have shown that the nuclei must *jump* (hence the term *surface jumping*). In Ref. [16] we farther developed this idea and applied it to a model of a radiationless transition in the Benzene molecule. In Ref. [14] we gave a complete analytic solution for finding the jumping point for a multidimensional harmonic model, and a perturbative solution for anharmonic potentials. In Ref. [18] we found the most likely division of energy between several identical accepting modes in a vibronic transition and compared the predictions of the phase-space surface-jumping method to exact quantum calculations. In our present work we have developed an approximation for the transition rate which is based on calculating the flow of probability between the two potential surfaces around the jumping point.

6. Conclusions

We studied Eq. (1) in the Wigner representation. Following Heller and Berry we have derived a useful classical limit for this equation and applied it to different systems. Predictions for a preferred mode of excitation or fragmentation in energy transfer processes in multidimensional complex systems are often needed. We have constructed a general framework for doing this for transitions where Fermi Golden Rule applies.

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