Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physics Letters A 327 (2004) 113–122
PHYSICS LETTERS A
www.elsevier.com/locate/pla

Quantum relaxation in hydrogen eigenstates and two-state transitions

C. Colijn, E.R. Vrscay *

Department of Applied Mathematics, University of Waterloo, Waterloo ON, N2L 3G1, Canada

Received 19 February 2004; received in revised form 30 April 2004; accepted 10 May 2004

Available online 19 May 2004

Communicated by P.R. Holland

Abstract

The evolution of probability distributions for quantum systems defined by the de Broglie–Bohm causal interpretation of quantum mechanics is examined in the context of whether, in general, a non-$|\psi|^2$ distribution will evolve to approximate a $|\psi|^2$ distribution, as has been suggested by Bohm and others. This study focusses on hydrogen eigenstates and two-state hydrogen transitions stimulated by semi-classical radiation. It is shown that this process of 'relaxation' will not in general occur in such hydrogen systems, and thus that the de Broglie–Bohm theory must retain the $|\psi|^2$ postulate if it is to be consistent with the standard quantum theory of individual systems.

PACS: 3.65.Bz

Keywords: De Broglie–Bohm quantum mechanics; Causal interpretation; Relaxation

1. Introduction

In the Schrödinger picture, the de Broglie–Bohm causal interpretation of quantum mechanics ascribes trajectories to quantum particles with spin according to the equation [4,10]

$$\mathbf{p} = \nabla S + \nabla(\log \rho) \times \mathbf{s}. \tag{1}$$

In this expression, the function S is proportional to the phase of the wave function

$$\psi = Re^{iS/\hbar},$$

$\rho = |\psi|^2$ is the magnitude squared of the wavefunction and $\mathbf{s}$ is the spin vector.[1]

It is now well known that the causal theory is consistent with standard quantum mechanics in the sense that if the initial distribution of positions is given by $P = |\psi|^2 = R^2$, then the continuity equation

$$\frac{\partial R^2}{\partial t} + \nabla \cdot \left(R^2 \frac{\nabla S}{m} \right) = 0 \tag{2}$$

* Corresponding author.
E-mail address: ervrscay@uwaterloo.ca (E.R. Vrscay).

[1] The original theory as stated by Bohm in [3] did not include the $\nabla \log \rho \times \mathbf{s}$ term; this turns out [10] to be necessary for consistency with a relativistic formulation.

0375-9601/$ – see front matter
doi:10.1016/j.physleta.2004.05.020

guarantees that the position distribution will remain consistent with $|\psi|^2$. Furthermore, the local values of other observables have been defined as functions of position in such as way as to yield consistency with standard quantum mechanics in the case that the positions are in agreement with the $|\psi|^2$ distribution [9]. Bohm and Hiley [4], as well as some others [15,16], have posed the question of what happens to a quantum system whose trajectories are defined according to the causal theory, when it does *not* start out in the standard $|\psi|^2$ distribution.

Bohm and Hiley argued in [4] that if the wave function is sufficiently complicated, the non-standard distribution will eventually approximate the $|\psi|^2$ distribution due to the spreading out of the trajectories. This has also been argued by Valentini, who used an analogue of the classical coarse-grained H-theorem [15,16]. Potel et al. have furthermore shown that when a quantum system is subject to noise in the de Broglie–Bohm theory, it will approach the $|\psi|^2$ distribution [12].

The $|\psi|^2$ distribution is a 'stable' one, in the sense that a distribution that is close to $|\psi|^2$ (in some appropriate metric) will continue to be close to $|\psi|^2$ due to the continuity equation [15,16]. As such, the approach to $|\psi|^2$ can be seen as a form of 'relaxation' to a quantum equilibrium. The 'equilibrium' state is defined as the situation where the spatial distribution is $|\psi|^2$; for this reason 'equilibrium' in this context does not imply that the distribution is constant in time, only that it is always (approximately) $|\psi|^2$, which itself is time-dependent in general.

Bohm and Hiley assume in [4] that the system is chaotic, and that each trajectory approaches each point in phase space arbitrarily closely at some time. Their relaxation argument makes use of this property. Valentini's 'subquantum H theorem' [15,16] admits the possibility that the coarse-grained H does not change, and thus that the distribution does not approach $|\psi|^2$; like the classical coarse-grained H theorem (see, for example, [14]), the approach to quantum equilibrium relies on both the coarse-graining and on the statistical nature of the system.

However, it is unclear exactly how complex the wave function needs to be in order to ensure that relaxation to quantum equilibrium will occur. It is also unclear on what time scale relaxation occurs, when it does. Bohm and Hiley were convinced that in the context of quantum statistical mechanics, quantum relaxation would ensure that the causal theory's postulate that the distribution of initial conditions is always $P = \rho = |\psi|^2$ would not be needed [4]. This reduction in the number of fundamental assumptions of the theory would be possible because even if the system started out in some arbitrary 'non-quantum' or non-$|\psi|^2$ distribution, the system's own time evolution would carry it to a distribution which would approximate $|\psi|^2$. Thereafter, the standard quantum mechanical predictions would be recovered.

Valentini has shown that if there were quantum systems with a non-standard (i.e., non-$|\psi|^2$) distribution, then they would behave very strangely. For example, they would violate the no-signalling rule [15–17] as well as other rules of quantum mechanics such as the uncertainty principle. Therefore, if there were systems which, for some reason, were unlikely to relax to quantum equilibrium, then the presence of the $|\psi|^2$ postulate in the causal theory would be necessary in order for the theory to make predictions consistent with standard quantum mechanics, and hence with experimental observation.

The question of relaxation in the deterministic de Broglie–Bohm theory is thus an important one. In this Letter we argue that there are physically meaningful systems for which quantum relaxation will not occur, and that if the causal theory is to describe individual systems (something which is considered one of its advantages [1]), then the $|\psi|^2$ postulate must be retained.

2. Relaxation in hydrogen eigenstates

We first argue that quantum relaxation will not occur in any of the standard hydrogen eigenstates under the Schrödinger, Pauli or Dirac equations.

Trajectories for hydrogen eigenstates were found in [5] and [7]. In [5] the eigenstates considered were the standard Schrödinger energy-angular momentum eigenstates, which are eigenstates of the energy, the orbital angular momentum L and the z-component of the orbital angular momentum, L_z. They are given by

$$\psi_{nlm} = N_{nlm} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) \times Y_l^m(\theta,\phi), \tag{3}$$

Table 1
Angular rates of revolution for hydrogen eigenstates

Schrödinger trajectories		Pauli/Dirac trajectories	
n, ℓ, m	$d\phi/dt$	n, ℓ, j, m	$d\phi/dt$
$1, 0, 0$	$\pm\frac{\hbar}{m_e ar}$	$1, 0, \frac{1}{2}, \pm\frac{1}{2}$	$\pm\frac{\hbar}{m_e ar}$
$2, 0, 0$	$\pm\frac{\hbar}{2m_e ar}\left(\frac{1}{1-\frac{r}{2a}}+1\right)$	$2, 0, \frac{1}{2}, \pm\frac{1}{2}$	$\pm\frac{\hbar}{2m_e ar}\left(\frac{1}{1-\frac{r}{2a}}+1\right)$
$2, 1, 0$	$\pm\frac{\hbar}{2m_e ar}$	$2, 1, \frac{3}{2}, \pm\frac{3}{2}$	$\pm\frac{\hbar}{2m_e ar}$
$2, 1, \pm1$	$\pm\frac{\hbar}{2m_e ar}$	$2, 1, \frac{1}{2}, \pm\frac{1}{2}$	$\pm\frac{\hbar}{m_e r^2}\left(3-\frac{r}{2a}\right)$
		$2, 1, \frac{3}{2}, \pm\frac{1}{2}$	$\pm\frac{\hbar}{2m_e ra}\frac{8\cos^2\theta-\sin^2\theta}{4\cos^2\theta+\sin^2\theta}$

where a is the Bohr radius, the L_{n-l-1}^{2l+1} are the associated Laguerre polynomials, and the $Y_l^m(\theta,\phi)$ are the spherical harmonics.[2] We use a spherical coordinate system in which θ is the angle measured down from the positive z axis, and ϕ is measured counter-clockwise from the positive x axis. For the moment, the form of the Laguerre polynomials is not relevant. For the Schrödinger equation it was assumed that the spin was constant and in either the positive or negative z direction.

The resulting trajectories for these eigenstates are all of the same form: circular motion about the z axis. The rates of revolution of the electron about the z axis depend on the eigenstate, i.e., on the quantum numbers n, ℓ, and m, and on the radius r and in some cases also the angle θ; these last are given by the initial condition.

Trajectories have also been determined [7] for hydrogen eigenstates resulting from the Pauli and Dirac equations. Here, the wavefunctions are eigenfunctions of the Hamiltonian H, the total angular momentum M^2 and the z component of the total angular momentum, M_z, with eigenvalues E_n, $\hbar^2 j(j+\frac{1}{2})$ and $\hbar m$, respectively.

In the Pauli case, it also happens that the orbital angular momentum operator L^2 commutes with the Hamiltonian. Thus, we are free to choose eigenstates which are eigenstates of L^2 with eigenvalue $\hbar^2\ell(\ell+1)$, as well as M^2. Because the Dirac eigenstates are constructed from the Pauli eigenstates (see [2] for a complete discussion of this matter), they are characterized by the quantum number ℓ though it is not strictly a good quantum number under the Dirac equation. The eigenstates for both the Pauli and Dirac wave functions are thus characterized by quantum numbers n, ℓ, j, and m, corresponding to the operators H, L^2, M^2 and M_z, with corresponding eigenvalues E, $\hbar^2\ell(\ell+1)$, $\hbar^2 j(j+\frac{1}{2})$ and $\hbar m$, respectively. Note also that the Pauli eigenstates are two-component spinors, and the Dirac eigenstates are four-component vector wave functions. Details of the computation of the causal trajectories resulting from these wavefunctions are given in [7]. In these cases no assumption regarding the electron's spin needs to be made, as the spin is now coupled to the orbital angular momentum.

For all of the Pauli and Dirac eigenstates, the trajectories are qualitatively the same as they are under the Schrödinger equation: they are circles about the z axis, with rates of revolution that depend on r and θ, but not ϕ. These rates of revolution are given in Table 1.

Consider the ground state hydrogen wave function; in the Schrödinger, Pauli and Dirac contexts, the electron trajectory is given by

$$\frac{d\phi}{dt} = \frac{\hbar}{m_e ar},$$

where m_e is the mass of the electron and a is again the Bohr radius. Under the Schrödinger equation, the

[2] We use the following convention for the spherical harmonics:

$$Y_{\ell m}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} P_{\ell m}(\cos\theta) e^{im\phi},$$

$$P_{\ell m}(x) = \sqrt{\frac{2\ell+1}{2}\frac{(\ell-m)!}{(\ell+m)!}}\frac{1}{2^\ell \ell!}(1-x^2)^{m/2} \times \frac{d^{\ell+m}}{dx^{(\ell+m)}}(x^2-1)^\ell, \quad m \geqslant 0,$$

$$P_{\ell,-m}(x) = (-1)^m P_{\ell m}(x), \quad m < 0. \tag{4}$$

ground state wave function

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

is symmetric in θ and ϕ and has an exponential decay in r, so that if a system had the initial distribution $P = |\psi|^2$, the radial distribution would show an exponential decay. Note that there is a small, but non-zero, probability of finding the particle very far from the nucleus of the atom.

Under the circular trajectory, the radius r is a constant of motion. Thus, if the initial distribution does not have an exponential decay in the radial distribution, then under time evolution, it cannot ever approach or even approximate an exponential decay; the radial distribution must remain constant. Therefore, there can be no full relaxation. The system will never approximate the $|\psi|^2$ distribution.

As an example, consider the initial distribution

$$P = \begin{cases} 0, & r < a, \\ C, & a < r < 2a, \\ 0, & 2a < r, \end{cases} \tag{5}$$

where the constant C is chosen such that the distribution is normalized. In this case, all trajectories will remain in the region $a < r < 2a$. The probability of finding the particle, at *any* later time, in the other regions is identically zero, and thus the distribution will never evolve so as to approximate $|\psi|^2$. In a similar way, θ is a constant of motion, and if all trajectories were initially in some finite range of θ values, or indeed were distributed in any way not consistent with the θ symmetry in $|\psi|^2$, then at any later time this inconsistency would remain and full relaxation would not occur.

Note that there might be some partial relaxation, for example, in the variable ϕ. Consider an initial distribution in which all the points have $0 < \phi(0) < \pi/2$, with a variety of radii. The different rates $\frac{d\phi}{dt} = \frac{\hbar}{m_e a r}$ will result in a 'spreading' in ϕ, and eventually, it is quite conceivable that the ϕ distribution will appear symmetric, as it is in a $|\psi|^2$ distribution. However, for the circular trajectory of the ground state, this limited process of relaxation will not result in the system approximating a $|\psi|^2$ distribution overall; if the system does not start with a flat distribution in θ and an exponentially decaying distribution in r, it will never attain these even approximately.

This argument applies to all of the circular hydrogen eigenstate trajectories given in Table 1. Because this includes the eigenstate trajectories from the Schrödinger equation as well as from the Pauli and Dirac equations, it is in some sense a very general result. Its implications are of some interest; clearly not *all* quantum systems will relax to the $|\psi|^2$ equilibrium, even in an approximate sense. The question of how much more complexity is needed in order to guarantee relaxation is still open. To examine whether the postulate that the initial distribution is always $|\psi|^2$ may be relinquished, and if so under what conditions, we examine the question of relaxation in some other simple systems.

3. Transitions in hydrogen

Though relaxation does not occur in hydrogen eigenstates, it is possible that introducing more complexity will allow relaxation to occur. The next most complex situation would be to consider linear combinations of two eigenstates; we do this in this section, considering eigenstates of the Schrödinger equation under Hamiltonians containing perturbation terms that model semi-classical radiation.

3.1. The $1s$–$2p_0$ transition

In [6], the trajectories for a transition between the Schrödinger $1s$ and $2p_0$ eigenstates were found, using a perturbing Hamiltonian that contained a z-polarized oscillating electric field representing semi-classical radiation, and assuming a constant spin in the z direction. The wave function

$$\psi(t) = c_a(t)\psi_{100}e^{-iE_1t/\hbar} + c_b(t)\psi_{210}e^{-iE_2t/\hbar} \tag{6}$$

is a linear combination of two eigenstate wave functions; the functions $c_a(t)$ and $c_b(t)$ are complex-valued functions of time. With this wave function, the trajectories are much more complex than in any of the eigenstate cases.

However, it was found that there is still a constant of motion. Trajectories lie on hyperboloids of revolution defined by rotating curves given by

$$\xi = \frac{2}{A\sin\theta - 1}, \quad A = \frac{2 + \xi_0}{\xi_0 \sin\theta_0} > 1$$

about the z axis. Here, ξ is the dimensionless variable r/a and A is the relevant constant of motion determined by the initial conditions. Each trajectory is constrained to lie on some hyperbola characterized by the number A. Within the hyperbolae of revolution the trajectories are quite complicated.

The existence of the invariant sets provides an answer to the question of whether a system undergoing the $1s$–$2p_0$ transition can relax to a $|\psi|^2$ distribution. Suppose that the initial distribution places all the trajectories in a 'rotated band' between two of the hyperbolae, for example, in the range $a < A < b$. This would be analogous to a step function distribution. The entire rotated band is preserved as the system evolves in time. With reference to (3), note that both ψ_{100} and ψ_{210} have an exponential decay in r which will dominate the radial dependence for sufficiently large values of r. Clearly, the preservation of *all* arbitrary rotated hyperbolic bands of the form $a < A < b$ will not be consistent with a $|\psi|^2$ distribution. Indeed, one does not need to choose a 'step' distribution in order to demonstrate this; any distribution without the same overall r dependence as $|\psi|^2$ will do.

Therefore, in the case of the $1s$–$2p_0$ transition, the presence of a non-trivial invariant set prevents full relaxation. A non-$|\psi|^2$ distribution will never relax to a $|\psi|^2$ distribution precisely because the trajectories cannot leave the invariant hyperbolae.

3.2. Other transitions in hydrogen

In this section, we show that the same kinds of invariant sets exist in other transitions in hydrogen. We consider radiation other than z-polarized radiation; if the perturbing Hamiltonian can have light polarized in any direction $\mathbf{r}$, then more transitions are 'allowed'.

In this context, a transition between two states $|\psi_a\rangle$ and $|\psi_b\rangle$ is 'allowed' if the matrix element $\langle\psi_a|H'|\psi_b\rangle$ is non-zero, where H' is the perturbing Hamiltonian. For semi-classical radiation, the perturbing Hamiltonian H' takes the form

$$H' = -e\mathbf{r}\cdot\mathbf{E}_o\cos(\omega t), \tag{7}$$

where e is the electric charge and $\mathbf{E}_o\cos(\omega t)$ is the oscillating electric field. We must therefore consider matrix elements of the form $\langle\psi_a|z|\psi_b\rangle$, $\langle\psi_a|x|\psi_b\rangle$ and $\langle\psi_a|y|\psi_b\rangle$. In this analysis it will be sufficient for our purposes to examine the structure of the equations that determine the causal trajectories; the presence of invariant sets can be investigated without specifying the field strength or perturbing frequency, and without finding the fully time-dependent trajectories.

It is well known [8,13] that there are selection rules governing which of the relevant matrix elements are non-zero, and thus which transitions are allowed. The only non-zero matrix elements involve pairs of wave functions such that the change in the quantum number m is either 0 or 1, and the change in ℓ is 1, i.e., $\Delta m = 0, \pm 1$ and $\Delta\ell = \pm 1$. There is no constraint on the change in n, though the frequency of the incoming radiation will affect which transitions are stimulated. We will, in this analysis, assume that only two-state transitions will occur, so that the wave function is always a linear combination of two eigenstate wavefunctions.

The task is now to compute the causal trajectories to a sufficient degree of detail to show that the allowed transitions give rise to the kind of invariant sets that occur in the $1s$–$2p_0$ transition. Once this has been done, the relaxation argument of Section 3.1 can be applied to show that in general, full relaxation will not occur in *any* of these hydrogen transition problems. If were are no such invariant sets, then it is possible that full relaxation to quantum equilibrium might occur.

To find the structure of the trajectories, we shall examine the structure of the terms ∇S and $\nabla\log\rho\times\mathbf{s}$, which compose the total momentum (see (1)). In order to do this, note that

$$\nabla S = \frac{\hbar}{\psi^*\psi}\,\mathrm{Im}\big\{(\nabla\psi)\psi^*\big\},$$
$$\nabla\log\rho = \frac{2}{\psi^*\psi}\,\mathrm{Re}\big\{(\nabla\psi)\psi^*\big\}, \tag{8}$$

so that in order to examine the structure of the resulting differential equations for the particle's momentum, we must examine $\mathrm{Im}\{(\nabla\psi)\psi^*\}$ and $\mathrm{Re}\{(\nabla\psi)\psi^*\}$. We shall be seeking a similarity in form among the r, θ and ϕ component equations.

We write the wave function as:

$$\psi = c_a(t)\psi_a + c_b(t)\psi_b, \tag{9}$$

where ψ_a and ψ_b are Schrödinger eigenstate wave functions and $c_a(t)$ and $c_b(t)$ are unspecified time-dependent coefficients which include the $e^{-iE_kt/\hbar}$ oscillations. This expresses our restriction to two-state transitions.

With reference to (3), we write the Schrödinger eigenfunctions as

$$\psi_{n\ell m} = R_{n\ell}(r) P_{\ell m}(\cos\theta) e^{im\phi}, \tag{10}$$

where the normalization constant (which is not critical here) is included in the radial function $R_{n\ell}(r)$. The important feature of these wave functions in this context is that their ϕ dependence is so simple. It will be necessary to examine the $\Delta m = 0$ and $\Delta m = 1$ transitions separately, as the relevant terms have somewhat different structures in the two cases.

3.2.1. Transitions in which $\Delta m = 0$

From (10), it is clear that if $m = 0$ in both wave functions, then there is no ϕ dependence in the total wave function (9). Thus, in this case, both $\mathrm{Im}\{(\nabla\psi)\psi^*\}$ and $\mathrm{Re}\{(\nabla\psi)\psi^*\}$ have no ϕ component. With reference to (8), this implies that transitions in which $m = 0$ in both ψ_a and ψ_b have the property that the ∇S term contributes only to the r and θ momentum. The $\nabla\log\rho\times\mathbf{s}$ term is perpendicular to both ρ and $\mathbf{s}$, and therefore is in the ϕ direction only. It is thus responsible only for the ϕ momentum.

Furthermore, if $m \neq 0$ but $\Delta m = 0$, then the ϕ component of $(\nabla\psi)\psi^*$ is simply $im\psi\psi^*/r\sin\theta$. This has no real part, so there is still no ϕ component of $\nabla\log\rho$, and the imaginary part is $m\psi\psi^*/r\sin\theta$. Thus the ∇S term now contributes $\frac{m\hbar}{r\sin\theta}$ to the ϕ component of the momentum. Because $\nabla\log\rho$ has no ϕ component, it is again the case that $\nabla\log\rho\times\mathbf{s}$ has *only* a ϕ component and does not contribute to either the r or θ momentum.

We must therefore examine the r and θ components of ∇S. Our goal is to show that they have sufficiently similar form that we can obtain from the momentum equation (1) a differential equation in r and θ only, whose solutions give an invariant set like that of the $1s$–$2p_0$ transition.

The radial part of $(\nabla\psi)\psi^*$ is given by

$$\frac{\partial\psi}{\partial r}\psi^* = \left(c_a\frac{\partial\psi_a}{\partial r} + c_b\frac{\partial\psi_b}{\partial r}\right)\left(c_a^*\psi_a^* + c_b^*\psi_b^*\right).$$

Expanding gives

$$\frac{\partial\psi}{\partial r}\psi^* = |c_a|^2\frac{\partial\psi_a}{\partial r}\psi_a^* + |c_b|^2\frac{\partial\psi_b}{\partial r}\psi_b^* + c_a c_b^*\frac{\partial\psi_a}{\partial r}\psi_b^* + c_a^* c_b\frac{\partial\psi_b}{\partial r}\psi_a^*. \tag{11}$$

The first two terms of (11) have no imaginary parts and so do not contribute to ∇S. In the last two terms of (11), note that $\frac{\partial\psi_a}{\partial r}\psi_b^*$ and $\frac{\partial\psi_b}{\partial r}\psi_a^*$ are real, because the only imaginary parts of the wavefunctions (see (10)) arise in the $e^{im\phi}$ term and here, we have assumed that $\Delta m = 0$ so that these terms always cancel.

The only imaginary terms thus come from $c_a c_b^*$ and $c_a^* c_b$ which are complex conjugates of each other. Therefore,

$$\mathrm{Im}\left\{\frac{\partial\psi}{\partial r}\psi^*\right\} = \mathrm{Im}\{c_a c_b^*\}\left(\frac{\partial\psi_a}{\partial r}\psi_b^* - \frac{\partial\psi_b}{\partial r}\psi_a^*\right). \tag{12}$$

The above expression is a function of time, $\mathrm{Im}\{c_a c_b^*\}$, times a function of r and θ only.

By a similar argument we find that

$$\mathrm{Im}\left\{\frac{1}{r}\frac{\partial\psi}{\partial\theta}\psi^*\right\} = \frac{1}{r}\mathrm{Im}\{c_a c_b^*\}\left(\frac{\partial\psi_a}{\partial\theta}\psi_b^* - \frac{\partial\psi_b}{\partial\theta}\psi_a^*\right). \tag{13}$$

This is a product of the same function of time as that which appears in (12), and a different function of r and θ only. In summary, the momentum terms for the $\Delta m = 0$ transitions from the ∇S contribution are:

$$p_r = \frac{\hbar}{\psi^*\psi}\mathrm{Im}\{c_a c_b^*\}\left(\frac{\partial\psi_a}{\partial r}\psi_b^* - \frac{\partial\psi_b}{\partial r}\psi_a^*\right),$$
$$p_\theta = \frac{\hbar}{\psi^*\psi}\frac{1}{r}\mathrm{Im}\{c_a c_b^*\}\left(\frac{\partial\psi_a}{\partial\theta}\psi_b^* - \frac{\partial\psi_b}{\partial\theta}\psi_a^*\right). \tag{14}$$

The ϕ component comes from the $\nabla\log\rho\times\mathbf{s}$ term in addition to the contribution from ∇S, and is given by

$$p_\phi = \frac{\hbar}{\psi^*\psi}\left(\mathrm{Re}\left\{\frac{1}{r}\frac{\partial\psi}{\partial\theta}\psi^*\right\}\cos\theta + \mathrm{Re}\left\{\frac{\partial\psi}{\partial r}\psi^*\right\}\sin\theta\right) + \frac{m\hbar}{r\sin\theta}. \tag{15}$$

This yields the system of differential equations:

$$\frac{dr}{dt} = \frac{\hbar}{m_e\psi^*\psi}\mathrm{Im}\{c_a c_b^*\}\left(\frac{\partial\psi_a}{\partial r}\psi_b^* - \frac{\partial\psi_b}{\partial r}\psi_a^*\right),$$
$$\frac{d\theta}{dt} = \frac{\hbar}{m_e\psi^*\psi}\frac{1}{r^2}\mathrm{Im}\{c_a c_b^*\}\left(\frac{\partial\psi_a}{\partial\theta}\psi_b^* - \frac{\partial\psi_b}{\partial\theta}\psi_a^*\right),$$
$$\frac{d\phi}{dt} = \frac{\hbar}{m_e\psi^*\psi}\frac{1}{r\sin\theta} \times\left(\mathrm{Re}\left\{\frac{1}{r}\frac{\partial\psi}{\partial\theta}\psi^*\right\}\cos\theta + \mathrm{Re}\left\{\frac{\partial\psi}{\partial r}\psi^*\right\}\sin\theta + m\right). \tag{16}$$

where we have used the relations $d\theta/dt = (1/m_e r)p_\theta$ and $d\phi/dt = (1/m_e r\sin\theta)p_\phi$.

Now, the first two differential equations are of very similar form. Indeed, we can write

$$\frac{dr}{d\theta} = r^2 \frac{\frac{\partial\psi_a}{\partial r}\psi_b^* - \frac{\partial\psi_b}{\partial r}\psi_a^*}{\frac{\partial\psi_a}{\partial\theta}\psi_b^* - \frac{\partial\psi_b}{\partial\theta}\psi_a^*} \tag{17}$$

from the first two equations. With reference to (10), this can be written

$$\frac{dr}{d\theta} = r^2 \frac{P_a P_b}{R_a R_b}\left(\frac{\frac{dR_a}{dr}R_b - \frac{dR_b}{dr}R_a}{\frac{dP_a}{d\theta}P_b - \frac{dP_b}{dd\theta}P_a}\right), \tag{18}$$

where a and b refer to the quantum numbers of ψ_a and ψ_b, respectively. Eq. (18) represents the desired r–θ curves and is valid when the denominator is non-zero. It will have a solution in some interval when the function on the right-hand side is continuous and when its partial derivative with respect to r is continuous.

The denominator of (18) vanishes when

$$\frac{\partial\psi_a}{\partial\theta}\psi_b^* - \frac{\partial\psi_b}{\partial\theta}\psi_a^* = 0.$$

From (10), it can be seen that this is equivalent to

$$R_a(r)R_b(r)\frac{dP_a(\cos\theta)}{d\theta}P_b(\cos\theta) - R_a(r)R_b(r)\frac{dP_b(\cos\theta)}{d\theta}P_a(\cos\theta) = 0.$$

This in turn reduces to

$$\frac{dP_a(\cos\theta)}{P_a} = \frac{dP_b(\cos\theta)}{P_b}$$

which implies, upon integration and exponentiation, that

$$P_a(\cos\theta) = K P_b(\cos\theta). \tag{19}$$

This will only be the case if $P_a = P_b$, or in other words, if the two states in the transition are in fact the same state: $\psi_a = \psi_b$. In this case, the system is in one of the eigenstates already considered in Section 2. Note that the term $R_a R_b$ is not identically zero; it vanishes at most at isolated points.

The entire denominator can, therefore, only vanish at isolated points, and not on an interval. These points correspond to asymptotes of the r–θ curves resulting from integration of (18), and do not change the fact that (18) has solutions for almost all initial conditions.

Such solutions define the required invariant sets—the invariant sets will be surfaces generated by rotating the r–θ curves generated by solving (18) about the z axis. This rotation is due to the ϕ component of the momentum. The r–θ curves can be explicitly computed in, for instance, the x–z plane; the surfaces formed by rotating the resulting curves about the z axis are invariant two-dimensional surfaces on which the trajectories must remain.

Thus, the same kind of structure as was seen in the $1s$–$2p_0$ transition happens in all of the $\Delta m = 0$ transitions. The integration of (18) will involve a constant of integration which will be a constant of motion, determined by the initial position. The distribution of this constant of motion is thus determined by the distribution of initial positions, and there is an implication for the question of relaxation: if the initial distribution does not distribute the constant of motion in a way that is consistent with the $|\psi|^2$ distribution, then full relaxation to the $|\psi|^2$ distribution cannot occur even in a coarse-grained sense, because trajectories can never leave the invariant surfaces.

3.2.2. *Transitions in which* $\Delta m = 1$

We now examine the ∇S and $\nabla\log\rho\times\mathbf{s}$ terms for transitions in which $\Delta m = 1$. We shall again show that the r and θ differential equations are of sufficiently similar form as to have the same dependence on both time and ϕ, so that their ratio defines $dr/d\theta$ as a function of r and θ. To do this, we will have to examine the r and θ components of both ∇S and $\nabla\log\rho\times\mathbf{s}$.

Beginning as usual with the r component of ∇S, we have the same expression as before, i.e., (11). But now, while the first two components are again real and thus do not contribute to ∇S (which involves only the imaginary part of $(\nabla\psi)\psi^*$), the second two terms are more complicated than before because the $e^{im\phi}$ terms no longer cancel.

We now have from (11)

$$\mathrm{Im}\left\{\frac{\partial\psi}{\partial r}\psi^*\right\} = \mathrm{Im}\left\{c_a c_b^*\frac{\partial\psi_a}{\partial r}\psi_b^* + c_a^* c_b\frac{\partial\psi_b}{\partial r}\psi_a^*\right\}, \tag{20}$$

and the only non-real term in the wave functions results from the ϕ dependence. Assuming without loss

of generality that $m_1 = m_2 + 1$, we have

$$\frac{\partial \psi_a}{\partial r}\psi_b^* = \frac{dR_a}{dr}R_b P_a P_b e^{i\phi},$$
$$\frac{\partial \psi_b}{\partial r}\psi_a^* = \frac{dR_b}{dr}R_a P_a P_b e^{-i\phi}, \tag{21}$$

which allows (21) to be written

$$\operatorname{Im}\left\{\frac{\partial \psi}{\partial r}\psi^*\right\} = \left(\frac{dR_a}{dr}R_b P_a P_b - \frac{dR_b}{dr}R_a P_a P_b\right) \times \left(\operatorname{Im}\{c_a c_b^*\}\cos\phi + \operatorname{Re}\{c_a c_b^*\}\sin\phi\right). \tag{22}$$

It is again the case that the first term is a function of r and θ only. The second term is a function of time and ϕ. To simplify the notation, let

$$H(\phi, t) = \operatorname{Im}\{c_a c_b^*\}\cos\phi + \operatorname{Re}\{c_a c_b^*\}\sin\phi$$

so that (22) becomes

$$\operatorname{Im}\left\{\frac{\partial \psi}{\partial r}\psi^*\right\} = \left(\frac{dR_a}{dr}R_b P_a P_b - \frac{dR_b}{dr}R_a P_a P_b\right) \times H(\phi, t). \tag{23}$$

It is necessary to see if a similar structure occurs in the θ component of ∇S, and also in the components of $\nabla \log\rho \times \mathbf{s}$.

The θ component of ∇S can be found in a similar manner as the r component. Applying the same approach gives

$$\operatorname{Im}\left\{\frac{1}{r}\frac{\partial \psi}{\partial \theta}\psi^*\right\} = \left(\frac{1}{r}\frac{dP_a}{d\theta}P_b R_a R_b - \frac{1}{r}\frac{dP_b}{d\theta}P_a R_a R_b\right) \times H(\phi, t). \tag{24}$$

This has the same time and ϕ dependence as the radial component in (23), and again the other factor is only a function of r and θ. Thus, the r and θ components of ∇S are given by

$$(\nabla S)_r = \frac{\hbar}{\psi^\dagger\psi}\operatorname{Im}\left\{\frac{\partial \psi}{\partial r}\psi^*\right\} = \frac{\hbar}{\psi^\dagger\psi}P_a P_b\left(\frac{dR_a}{dr}R_b - \frac{dR_b}{dr}R_a\right)H(\phi, t),$$
$$(\nabla S)_\theta = \frac{\hbar}{\psi^\dagger\psi}\operatorname{Im}\left\{\frac{1}{r}\frac{\partial \psi}{\partial \theta}\psi^*\right\} = \frac{\hbar}{\psi^\dagger\psi}\frac{R_a R_b}{r}\left(\frac{dP_a}{d\theta}P_b - \frac{dP_b}{d\theta}P_a\right) \times H(\phi, t). \tag{25}$$

The r and θ components of ∇S have sufficiently similar structure as to define $dr/d\theta$ as a function of r and θ only, which is ultimately what we require. However, unlike in the $\Delta m = 0$ transitions, the term $\nabla \log\rho \times \mathbf{s}$ now does not necessarily only have a ϕ component. In fact, it now has all three components, so the r and θ components found in (25) contain only part of the total r and θ momentum.

In the $\Delta m = 0$ transitions, recall that $\nabla \log\rho \times \mathbf{s}$ had only a ϕ component because the ϕ component of $\nabla \log\rho$ was zero. This was because the ϕ component of $(\nabla\psi)\psi^*$ had no real parts, and because we are assuming that the spin vector is in the $\hat{k}$ direction so that the spin is given by $\mathbf{s} = \cos\theta\hat{\theta} - \sin\theta\hat{r}$. For simplicity of notation, let

$$A \equiv \nabla \log\rho;$$

the desired cross product can be written

$$\nabla \log\rho \times \mathbf{s} = \frac{\hbar}{2}\begin{vmatrix} \hat{\theta} & \hat{\phi} & \hat{r} \\ A_\theta & A_\phi & A_r \\ \cos\theta & 0 & -\sin\theta \end{vmatrix}. \tag{26}$$

Thus, to find the r and θ components of $\nabla \log\rho \times \mathbf{s}$ it is necessary only to find A_ϕ, which, from (8), can be done by finding the ϕ component of $\operatorname{Re}\{(\nabla\psi)\psi^*\}$. This is given by

$$\operatorname{Re}\left\{\frac{1}{r\sin\theta}\frac{\partial \psi}{\partial \phi}\psi^*\right\} = \frac{1}{r\sin\theta}\operatorname{Re}\{(im_1 c_a\psi_a + im_2 c_b\psi_b) \times (c_a^*\psi_a^* + c_b^*\psi_b^*)\} = -\frac{1}{r\sin\theta}\operatorname{Im}\{c_a c_b^* m_1\psi_a\psi_b^* + c_a^* c_b m_2\psi_a^*\psi_b\}. \tag{27}$$

Because we assumed that $m_1 = m_2 + 1$, this can be simplified using the fact that

$$\psi_a\psi_b^* = R_a R_b P_a P_b e^{i\phi},$$
$$\psi_b\psi_a^* = R_a R_b P_a P_b e^{-i\phi}, \tag{28}$$

and the above becomes

$$\operatorname{Re}\left\{\frac{1}{r\sin\theta}\frac{\partial \psi}{\partial \phi}\psi^*\right\} = -\frac{R_a R_b P_a P_b}{r\sin\theta} \times \left(\operatorname{Re}\{c_a c_b^*\}\sin\phi + \operatorname{Im}\{c_a c_b^*\}\cos\phi\right). \tag{29}$$

The term we are seeking, A_ϕ, is therefore given by

$$A_\phi = \frac{2}{\psi^*\psi}\left(-\frac{R_a R_b P_a P_b}{r\sin\theta}\right) \times \left(\mathrm{Re}\{c_a c_b^*\}\sin\phi + \mathrm{Im}\{c_a c_b^*\}\cos\phi\right) = -\frac{2}{\psi^*\psi}\left(\frac{R_a R_b P_a P_b}{r\sin\theta}\right) H(\phi,t). \quad (30)$$

Note that this is the same time and ϕ dependence $H(\phi,t)$ that occurs in the r and θ terms of ∇S.

The r and θ components of $\nabla\log\rho\times\mathbf{s}$ are hence given by

$$(\nabla\log\rho\times\mathbf{s})_r = -A_\phi s_\theta = -\frac{1}{r}\frac{\hbar}{\psi^*\psi} R_a R_b P_a P_b H(\phi,t) \quad (31)$$

and

$$(\nabla\log\rho\times\mathbf{s})_\theta = -A_\phi s_r = -\frac{1}{r}\cot\theta\frac{\hbar}{\psi^*\psi} R_a R_b P_a P_b H(\phi,t). \quad (32)$$

Now we can find the r and θ components of the total momentum using (1), (25) and the above:

$$p_r = (\nabla S)_r + (\nabla\log\rho\times\mathbf{s})_r = \frac{\hbar}{\psi^*\psi} P_a P_b\left(\frac{dR_a}{dr}R_b - \frac{dR_b}{dr}R_a - \frac{R_a R_b}{r}\right) \times H(\phi,t),$$

$$p_\theta = (\nabla S)_\theta + (\nabla\log\rho\times\mathbf{s})_\theta = \frac{\hbar}{\psi^*\psi}\frac{R_a R_b}{r}\left(\frac{dP_a}{d\theta}P_b - \frac{dP_b}{d\theta}P_a - P_a P_b\cot\theta\right) \times H(\phi,t). \quad (33)$$

This corresponds to the system of differential equations

$$\frac{dr}{dt} = \frac{\hbar}{m_e\psi^*\psi} P_a P_b\left(\frac{dR_a}{dr}R_b - \frac{dR_b}{dr}R_a - \frac{R_a R_b}{r}\right) \times H(\phi,t),$$

$$\frac{d\theta}{dt} = \frac{\hbar}{m_e r^2\psi^*\psi} R_a R_b \times \left(\frac{dP_a}{d\theta}P_b - \frac{dP_b}{d\theta}P_a - P_a P_b\cot\theta\right) \times H(\phi,t), \quad (34)$$

where it should be understood that we have left the ϕ differential equation out because it is not relevant to the question of whether the r and θ components have sufficiently similar structure to give rise to invariant sets of the kind seen previously.

Indeed, the above result shows that they do have sufficient structure. Dividing the two equations of (34) gives

$$\frac{dr}{d\theta} = r^2\frac{P_a P_b}{R_a R_b}\frac{(\frac{dR_a}{dr}R_b - \frac{dR_b}{dr}R_a - \frac{R_a R_b}{r})}{(\frac{dP_a}{d\theta}P_b - \frac{dP_b}{d\theta}P_a - P_a P_b\cot\theta)}. \quad (35)$$

This is a separable equation whose solutions $r(\theta)$ contain a constant of integration determined by the initial condition. It will have solutions when the denominator is non-zero. As in the case of (18), this condition is satisfied by almost all points in the space, for the equation

$$\frac{dP_a}{d\theta}P_b - \frac{dP_b}{d\theta}P_a - P_a P_b\cot\theta$$

can be integrated and exponentiated, yielding the condition

$$\frac{P_a}{P_b} = A\sin\theta. \quad (36)$$

When this relation holds on an interval, rather than at specific points, it holds identically for $\theta\in[0,\pi]$. In this case, θ *itself* is the constant of motion we seek. If

$$\frac{d\theta}{dt} = 0$$

on the trajectories, then the motion is constrained to cone-shaped surfaces. In general, the $r(\theta)$ curves given by (35) are rotated about the z axis as ϕ changes in a manner determined by the ϕ differential equation (which we have not written explicitly). The resulting surfaces are invariant.

Both (18) and (35) give rise to non-trivial invariant sets characterized by constants of motion that are determined by initial conditions. Thus, in both cases, if the relevant constants are not initially distributed in a manner consistent with the $|\psi|^2$ distribution, then at later times the overall distribution will not necessarily approach $|\psi|^2$, for the reasons given in the last section.

4. Conclusions

We have considered eigenstates of hydrogen under the Schrödinger, Pauli and Dirac equations, as well

as two-state transitions stimulated by semi-classical radiation. In our transition problems, the transition occurs between two Schrödinger eigenstates and the spin is assumed to be constant and in the positive z direction. In all of these situations, if the initial distribution is such that the constant of motion is not distributed as it would be in a $|\psi|^2$ distribution, then because the trajectories are constrained to remain on invariant surfaces, the distribution will not evolve so as to approximate a $|\psi|^2$ distribution.

Thus, the process of quantum relaxation posited by Valentini in [15,16] and by Bohm and Hiley in [4] does not occur in these systems; no matter how long they are left to pursue their natural time evolution, a non-$|\psi|^2$ distribution of positions will not evolve to approximate a $|\psi|^2$ distribution. This does not contradict the subquantum H theorem of Valentini, because that theorem simply guarantees that the derivative of the coarse-grained H function, dH/dt, satisfies

$$\frac{dH}{dt} \leqslant 0,$$

where H decreases to zero as the distribution approaches $|\psi|^2$. In the systems considered in this Letter, H could be constant, or could decrease but not approach a limit of zero. This would be consistent with the H theorem, but the system would not necessarily approach the $|\psi|^2$ distribution. Furthermore, the systems considered here, while physically meaningful, are not chaotic or ergodic and an argument such as Bohm and Hiley's would not apply. In the absence of invariant sets and constants of motion, quantum relaxation would likely occur; however, Bohm and Hiley's argument does not prove this, as they assume ergodic dynamics and discuss only a particle in a box [4].

One could argue that eigenstates, as well as the transitions that we have described, represent very simple systems. Our transition problem assumes that the spin is constant, which is an approximation. The Schrödinger equation is non-relativistic, and furthermore, the semi-classical representation of radiation is an approximation of a more complicated interaction that would involve the magnetic field, a full description of the photons as quanta, etc. It is by no means guaranteed, however, that these systems would not have constants of motion analogous to the ones found here. It remains the case that for the range of physical systems considered here, which are typically used as descriptions of hydrogen eigenstates and transitions in standard texts on quantum mechanics (see, for example, [8,11,13]), quantum relaxation cannot be relied upon to produce a $|\psi|^2$ distribution of positions.

This is in some sense a powerful conclusion, for it addresses the question of whether the initial $|\psi|^2$ distribution is a necessary postulate of the de Broglie–Bohm theory. These results indicate that it *is* a necessary postulate, for there are physically meaningful situations in which an arbitrary initial distribution will not 'naturally' evolve in time to approximate a $|\psi|^2$ distribution as has been claimed.

References

[1] J.S. Bell, Speakable and Unspeakable in Quantum Mechanics, Cambridge Univ. Press, Cambridge, 1987.
[2] H. Bethe, E. Salpeter, Quantum Mechanics of One- and Two-Electron Systems, Springer, 1957.
[3] D. Bohm, Phys. Rev. 85 (1952) 166.
[4] D. Bohm, B.J. Hiley, The Undivided Universe, Routledge, London, 1993.
[5] C. Colijn, E.R. Vrscay, Phys. Lett. A 300 (5–6) (2002) 334.
[6] C. Colijn, E.R. Vrscay, J. Phys. A: Math. Gen. 36 (2003) 4689.
[7] C. Colijn, E.R. Vrscay, Found. Phys. Lett. 16 (4) (2003) 303.
[8] D. Griffiths, Introduction to Quantum Mechanics, Prentice Hall, Englewood Cliffs, NJ, 1995.
[9] P. Holland, The Quantum Theory of Motion, Cambridge Univ. Press, Cambridge, 1993.
[10] P. Holland, Phys. Rev. A 60 (6) (1999).
[11] A. Messiah, Quantum Mechanics, North-Holland, Amsterdam, 1961.
[12] G. Potel, M. Munoz-Alenar, F. Barranco, E. Vigezzi, Phys. Lett. A 299 (2002).
[13] L. Schiff, Quantum Mechanics, McGraw–Hill, New York, 1955.
[14] D. ter Haar, Elements of Statistical Mechanics, Rinehart, New York, 1956.
[15] A. Valentini, Phys. Lett. A. 156 (1–2) (1991) 5.
[16] A. Valentini, Phys. Lett. A. 158 (1–2) (1991) 1.
[17] A. Valentini, J. Phys. (2002) 269.