About the proof that the s-wave functions of the hydrogen atom obey the Ehrenfest equation of motion

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Abstract. Applying the concept of quantum hydrodynamics on a hydrogen atom, one can derive an equation of motion which describes the time derivative of the mass current density for the relative motion of the electron and the proton. Since this derivation can be performed with the Ehrenfest theorem, we call this equation the Ehrenfest equation of motion. As quantum hydrodynamics is consistent with Schrödinger's quantum mechanics, the stationary s-wave functions satisfy both the Schrödinger equation and the Ehrenfest equation of motion. It is the purpose of this paper to prove that the stationary s-wave functions satisfy the Ehrenfest equation of motion. From the quantum hydrodynamical point of view, this result for s-wave functions can be interpreted that the Coulomb force density that attracts the electron to the proton is compensated by a quantum force density that is related to the dispersion of the probability density.

1. Introduction

The concept of quantum hydrodynamics (QHD) for one-electron systems was introduced by Madelung and Bohm [1–3]. Besides other authors, QHD was developed further by Epstein and Wyatt [4,5]. In Refs. [4,5], an equation is discussed that is related to the momentum balance of the system. Since the derivation of this momentum balance equation can be performed by calculating the time derivative of the mass current density with the Ehrenfest theorem [6], we call this equation the Ehrenfest equation of motion (EEM); it is given by

$$\frac{\partial \vec{j}_m}{\partial t} + \nabla \underline{\underline{\Pi}} \quad = \quad \vec{f}. \tag{1}$$

2. System

We analyse below a hydrogen atom in a spherical coordinate system where its origin is located at the center of mass of the atom. For this system, the quantities appearing in equation (1) – these are the Coulomb force density $\vec{f}$, the divergence of the momentum flow density tensor $\nabla \underline{\underline{\Pi}}$, and the mass current density $\vec{j}_m$ – refer to the relative motion of the electron and the proton.

In the following, the proof is shown that all s-wave functions Ψ_n of the hydrogen atom with the principal quantum number $n = 1, 2, 3, \ldots$ satisfy the EEM (1). This is a generalization of the calculations in [7], where this proof was performed explicitly for the 1s and the 2s wave

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functions. Since the s-wave functions are real-valued, $\vec{j}_m$ vanishes

$$\vec{j}_m \;=\; \vec{0}. \tag{2}$$

The Coulomb force density is given by

$$\vec{f} \;=\; -D\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2}\vec{e}_r. \tag{3}$$

Here, e is the elementary charge, ε_0 is the electric constant, and $D = |\Psi_n|^2$ is the probability density of finding the electron and the proton at the relative position $\vec{r} = \vec{r}_e - \vec{r}_p$, where $\vec{r}_e$ and $\vec{r}_p$ are the electron's and proton's positions. Then, $r = |\vec{r}|$ is both the electron-proton distance and the radius in the mentioned spherical coordinate system, and the vector $\vec{e}_r$ is the radial unit vector in this system. As the next step, we calculate $\nabla\underline{\underline{\Pi}}$.

We can split up the momentum flow density tensor $\underline{\underline{\Pi}}$ into the classical tensor $\underline{\underline{\Pi}}^{\mathrm{Cl}}$, the osmotical tensor $\underline{\underline{\Pi}}^{\mathrm{Os}}$, and the product of the unit matrix $\underline{1}$ and the scalar pressure P [5]

$$\underline{\underline{\Pi}} \;=\; \underline{\underline{\Pi}}^{\mathrm{Cl}} + \underline{\underline{\Pi}}^{\mathrm{Os}} + \underline{1}P. \tag{4}$$

The motivation for the naming of the classical tensor $\underline{\underline{\Pi}}^{\mathrm{Cl}}$ is that if the physical system is described by pure classical physics then equation (4) becomes $\underline{\underline{\Pi}} = \underline{\underline{\Pi}}^{\mathrm{Cl}}$. In contrast, both the osmotical tensor $\underline{\underline{\Pi}}^{\mathrm{Os}}$ and the scalar pressure P are related to the dispersion of the quantum wave packet and they are pure quantum quantities.
The classical tensor $\underline{\underline{\Pi}}^{\mathrm{Cl}}$ is given by

$$\underline{\underline{\Pi}}^{\mathrm{Cl}} \;=\; m_\mu D(\vec{v}\otimes\vec{v}), \tag{5}$$

where $m_\mu = m_{\mathrm{e}}m_{\mathrm{p}}/(m_{\mathrm{e}} + m_{\mathrm{p}})$ is the reduced mass of the electron (with the mass m_{e}) and the proton (with the mass m_{p}), and the term $\vec{v}\otimes\vec{v}$ is a dyadic product of the relative velocity $\vec{v}$ of the two particles. As the mass current density $\vec{j}_m$ is related to this velocity $\vec{v}$ by $\vec{j}_m = m_\mu D\vec{v}$, both of them vanish for the analyzed system – so, the classical tensor $\underline{\underline{\Pi}}^{\mathrm{Cl}}$ vanishes, too.
Moreover, the osmotical tensor $\underline{\underline{\Pi}}^{\mathrm{Os}}$ is given by

$$\underline{\underline{\Pi}}^{\mathrm{Os}} \;=\; m_\mu D(\vec{d}\otimes\vec{d}). \tag{6}$$

In the equation above, a dyadic product of the osmotic velocity $\vec{d}$, defined by

$$\vec{d} \;=\; -\frac{\hbar}{2m_\mu}\frac{\nabla D}{D}, \tag{7}$$

appears. In our spherical coordinate system, the s-wave functions Ψ_n depend only on the radius r, and not on the angles ϑ and φ. So, it holds for the probability density D, too. Thus, only the radial component d_r of the osmotical velocity does not vanish, and therefore only the Π_{rr}^{Os}-component of the tensor $\underline{\underline{\Pi}}^{\mathrm{Os}}$ is not zero. The result for this tensor component Π_{rr}^{Os} is

$$\Pi_{rr}^{\mathrm{Os}} \;=\; \frac{\hbar^2}{4m_\mu}\frac{1}{D}\left(\frac{\partial D}{\partial r}\right)^2. \tag{8}$$

The scalar pressure P is given by

$$P \;=\; -\frac{\hbar^2}{4m_\mu}\triangle D = -\frac{\hbar^2}{4m_\mu}\left(\frac{2}{r}\frac{\partial D}{\partial r} + \frac{\partial^2 D}{\partial r^2}\right). \tag{9}$$

Due to equation (4) and the disappearance of the classical tensor $\underline{\underline{\Pi}}^{\text{Cl}}$, we have to sum up the two tensor divergence terms $\nabla\underline{\underline{\Pi}}^{\text{Os}}$ and $\nabla(\underline{1}P)$ for the calculation of $\nabla\underline{\underline{\Pi}}$. By regarding how to calculate tensor divergences in spherical coordinates [8] and by taking into account equations (8) and (9), finally, we get:

$$\nabla\underline{\underline{\Pi}} = -\frac{\hbar^2}{4m_\mu}\left\{\frac{1}{D}\frac{\partial D}{\partial r}\left[\frac{1}{D}\left(\frac{\partial D}{\partial r}\right)^2 - \frac{2}{r}\frac{\partial D}{\partial r} - 2\frac{\partial^2 D}{\partial r^2}\right] - \frac{2}{r^2}\frac{\partial D}{\partial r} + \frac{2}{r}\frac{\partial^2 D}{\partial r^2} + \frac{\partial^3 D}{\partial r^3}\right\}\vec{e}_r. \quad (10)$$

As the next step, we multiply the EEM (1) with the vector $-\frac{4m_\mu}{\hbar^2}\vec{e}_r$ and use the results (equations (2), (3) and (10)) of the mass current density $\vec{j}_m$, the Coulomb force density $\vec{f}$ and the divergence of the momentum flow density tensor $\nabla\underline{\underline{\Pi}}$. In addition, we regard that the modified Bohr radius for a finite nuclear mass is given by $a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{m_\mu e^2}$. Then, we get this differential equation:

$$\frac{1}{D}\frac{\partial D}{\partial r}\left[\frac{1}{D}\left(\frac{\partial D}{\partial r}\right)^2 - \frac{2}{r}\frac{\partial D}{\partial r} - 2\frac{\partial^2 D}{\partial r^2}\right] - \frac{2}{r^2}\frac{\partial D}{\partial r} + \frac{2}{r}\frac{\partial^2 D}{\partial r^2} + \frac{\partial^3 D}{\partial r^3} = \frac{4}{a_\mu r^2}D. \quad (11)$$

3. Proof

Now, we show that this differential equation is solved by the quantum textbook result for stationary s-wave functions Ψ_n with the principal quantum number $n = 1, 2, 3, \ldots$ (see e.g. [9]). Therefore, we introduce a parameter $\lambda = \frac{2}{na_\mu}$ and a dimensionless coordinate $\rho = \lambda r$. The mentioned quantum textbook result for Ψ_n is

$$\Psi_n(\rho) = C\, g(\rho)\, \exp\left(-\frac{\rho}{2}\right), \quad (12)$$

where C is a real prefactor independent of the coordinate ρ. In addition, $g(\rho)$ is equal to the associated Laguerre polynomial $L_n^1(\rho)$ that satisfies this differential equation [9]:

$$\rho\frac{\partial^2 L_n^1(\rho)}{\partial\rho^2} + (2-\rho)\frac{\partial L_n^1(\rho)}{\partial\rho} + (n-1)L_n^1(\rho) = 0. \quad (13)$$

Therefore, the probability density D is given by

$$D(\rho) = C^2\,[g(\rho)]^2\,\exp(-\rho). \quad (14)$$

As the next step, we handle equation (14) as an ansatz for $D(\rho)$ and insert it into the differential equation (11). After some straightforward transformations, we find the differential equation for $g(\rho)$,

$$g\frac{\partial^3 g}{\partial\rho^3} + \left(1 - \frac{2}{\rho}\right)\left(\frac{\partial g}{\partial\rho}\right)^2 - \frac{\partial g}{\partial\rho}\frac{\partial^2 g}{\partial\rho^2} + \left(\frac{2}{\rho} - 1\right)g\frac{\partial^2 g}{\partial\rho^2} - \frac{2g}{\rho^2}\frac{\partial g}{\partial\rho} - \frac{n-1}{\rho^2}g^2 = 0, \quad (15)$$

and define

$$y(\rho) := \rho\frac{\partial^2 g}{\partial\rho^2} + (2-\rho)\frac{\partial g}{\partial\rho} + (n-1)g, \quad (16)$$

where, according to equation (13), the solution of $y(\rho) = 0$ is $g(\rho) = L_n^1(\rho)$, and

$$h(\rho) := \frac{y}{\rho}. \quad (17)$$

Now, we evaluate

$$
\begin{aligned}
g\frac{\partial h}{\partial \rho} &= g\frac{\partial}{\partial \rho}\left[\frac{\partial^2 g}{\partial \rho^2}+\left(\frac{2}{\rho}-1\right)\frac{\partial g}{\partial \rho}+\frac{n-1}{\rho}g\right], \\
&= g\frac{\partial^3 g}{\partial \rho^3}+\left(\frac{2}{\rho}-1\right)g\frac{\partial^2 g}{\partial \rho^2}-\frac{2g}{\rho^2}\frac{\partial g}{\partial \rho}+\frac{n-1}{\rho}g\frac{\partial g}{\partial \rho}-\frac{n-1}{\rho^2}g^2,
\end{aligned}
\tag{18}
$$

and

$$
\begin{aligned}
-\frac{\partial g}{\partial \rho}h &= -\frac{\partial g}{\partial \rho}\left[\frac{\partial^2 g}{\partial \rho^2}+\left(\frac{2}{\rho}-1\right)\frac{\partial g}{\partial \rho}+\frac{n-1}{\rho}g\right], \\
&= -\frac{\partial g}{\partial \rho}\frac{\partial^2 g}{\partial \rho^2}+\left(1-\frac{2}{\rho}\right)\left(\frac{\partial g}{\partial \rho}\right)^2-\frac{n-1}{\rho}g\frac{\partial g}{\partial \rho}.
\end{aligned}
\tag{19}
$$

Combining equations (18) and (19), the differential equation (15) is rewritten as

$$
g\frac{\partial h}{\partial \rho}-\frac{\partial g}{\partial \rho}h = 0,
\tag{20}
$$

or simply

$$
g\frac{\partial h}{\partial \rho} = \frac{\partial g}{\partial \rho}h.
\tag{21}
$$

Now, we can use the new version (21) of the differential equation (15) for $g(\rho)$ to prove that $g(\rho) = L_n^1(\rho)$ solves this differential equation (15). It is trivial that $h(\rho) = 0$ solves equation (21), and then $y(\rho) = \rho h(\rho) = 0$ is true. So, we have shown that $g(\rho) = L_n^1(\rho)$ solves (15) and, as a consequence, we have shown that the quantum textbook result for Ψ_n is a solution of the EEM (1), too.

4. Discussion

The fact that the s-wave functions Ψ_n satisfy the EEM means that these wave functions have such a form that the Coulomb force density, $\vec{f}$, that attracts the electron to the proton, and the divergence of the momentum flow density tensor, $\nabla\underline{\underline{\Pi}}$, that is related to the dispersion of the probability density, are consistent. Hereby, since only the quantum quantities $\underline{\underline{\Pi}}^{\mathrm{Os}}$ and P contribute to the tensor $\underline{\underline{\Pi}}$, the term $\nabla\underline{\underline{\Pi}}$ can be interpreted as a pure quantum force density.

The arguments presented in this paper advance a new view of the properties of the s-wave functions Ψ_n that are obtained by the analysis of the EEM.

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