On the classical treatment of the Stark effect in hydrogen atoms

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Summary. — A classical model of the hydrogen atom in a static electric field is studied, basing upon the work [Hooker A. et al, Phys. Rev. A, 55 (1997) 4609]. In that work the electrons are supposed to move along Kepler orbits around the nucleus, while interacting with the external field. That classical model reproduces very well the true energy shift of the linear Stark effect. The agreement with the second order effect is poor. It is shown here that the results for the quadratic Stark effect may be considerably improved if the electrons are still allowed to move along classical trajectories, but whose initial conditions are statistically sampled from a distribution resembling the quantum mechanical one.

PACS 32.60.+i - Zeeman and Stark effects.
PACS 32.10.Dk - Electric and magnetic moments, polarizability.
PACS 03.20.+i - Classical mechanics of discrete systems: general mathematical aspects

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1. - Introduction

The use of classical models to study quantum mechanical systems is largely employed in microscopic physics. For large quantum numbers it is justified on the basis of the correspondence principle. Also at small quantum numbers its utility is not negligible since it allows at least to obtain a qualitative insight of the dynamics of the system; in the best cases, it is even possible to extract quantitative results in an easy way and with a good accuracy. Some examples are the scattering of electrons from an atom [1, 2], and the treatment of energetic ion–atom collisions [3, 4, 5]. Classical models are obviously favoured over their quantum–mechanical counterparts from the numerical point of view. In those cases where also the quantum problem is solvable, the classical picture is important since it allows to clearly visualize the problem at hand. For these reasons the correspondence between the classical and quantum mechanical descriptions is currently a well studied topic.

Quite recently it has been proposed a purely classical view to the Stark effect in hydrogen [6]: the field is supposed to interact with classical electrons following Kepler orbits around the nucleus. Following this work, in ref. [7] the energy shifts for the linear and quadratic Stark effect have been computed. The agreement between the classical result and the exact quantum mechanical one is excellent for the linear effect but is not good for the quadratic effect, which only asymptotically for large quantum numbers approaches the correct value.

The purpose of the present paper is to show that, within a purely classical formalism very similar to that of [7], the quadratic Stark effect may be reproduced very accurately: it is enough to relax the bounds on the electron trajectory and adopt a statistical approach: here, the electron is still modelled as a classical particle following Kepler orbits but the initial conditions

\[ \text{It must be stressed that any "classical" model necessarily incorporates some elements of the quantum theory in order to simulate a microscopic object. The relevance of the approach of the present paper is that only initial conditions are to be chosen compatible with the laws of quantum mechanics.} \]
are picked up from a distribution subject to certain rules. It will be shown that a much better agreement is obtained by this slightly more sophisticated approach.

Atomic units will be used throughout this work unless explicitly stated.

2. - The classical model of [7]

As well known, the study of the Stark effect is easily performed in parabolic coordinates, where the hydrogen atom is classified by the quantum numbers $n, n_1, n_2, m$. We are considering small fields, for which a perturbative approach is adequate and they still are good quantum numbers.

I will first briefly summarize the treatment of the first-order Stark effect, which will be useful also to introduce the main concepts used later. First of all, let us recall some results stated in [6]. In that work a correspondence has been done between the quantum mechanical operators and their classical counterparts:

• to each set of values $n_1, n_2, n, m$ there corresponds a set of classical Keplerian orbits of the electron which are generally elliptical, with eccentricity $\varepsilon = \sqrt{1 - l^2/n^2}$ ($l$ is angular quantum number in spherical coordinates, and the classical angular momentum). When time-averaged over a period of rotation, the ellipse yields a non zero mean electric dipole moment:

$$< d > = \frac{1}{T} \int_0^T z \, dt = \frac{3}{2} n^2 \varepsilon .$$

• The Lenz vector $\mathbf{A} = \mathbf{p} \times \mathbf{L} - \mathbf{r}/|\mathbf{r}|$ is classically a conserved quantity, as is its $z$-component in quantum mechanics:

$$A_z = (n_1 - n_2)n .$$

$A$ is related to the electron orbit by $|\mathbf{A}| = \varepsilon$. Since, besides this, in [6] it was shown that $\mathbf{d}$ and $\mathbf{A}$ point towards the same direction, one may
identify them through

\[ d = (3/2)n^2 A \]  \hspace{1cm} (3) 

- The energy shift in presence of an electric field \( \mathbf{F} \) is calculated from

\[ \Delta E^{(1)} = -d \cdot \mathbf{F} \]  \hspace{1cm} (4)

It is immediate to see that this result agrees with the energy shift obtained using quantum mechanics [8] provided we use for \( d \) its form \( (3) \) with \( A \) given by \( (2) \):

\[ \Delta E^{(1)} = -\frac{3}{2}n(n_1 - n_2)|F| \]  \hspace{1cm} (5)

In [7] it was verified by numerically integrating the Kepler orbits in presence of an electric field and with initial conditions compatible with the quantized value \( (2) \) that the classical energy shifts from its unperturbed value of the quantity \( (3) \).

The quadratic effect is of relevance when \( n_1 = n_2 \), in which case the linear term vanishes. This means—in the language of [8]—that the mean dipole moment vanishes, and this happens when the orbits are circular and lying on a plane perpendicular to the field axis. The electric field may induce a dipole moment by shifting the electron and the nucleus with respect to each other. The energy shift for the quadratic Stark effect is defined by

\[ \Delta E^{(2)} \equiv -\frac{1}{2} \alpha F^2 \]  \hspace{1cm} (6)

\( \alpha \) being the polarizability. \( \alpha \) is related to the induced dipole moment by

\[ \alpha \mathbf{F} = d \]  \hspace{1cm} (7)

The quantum mechanical value of \( \alpha \) for states with \( n_1 = n_2 \) and \( m = n - 1 \) is [8]

\[ \alpha_{QM} = \frac{n^4}{4} \left(4n^2 + 9n + 5\right) \]  \hspace{1cm} (8)
In [7] a simple approximation is used to compute the classical value of \( \alpha \), \( \alpha_{cl} \): be \( r \) the radius of the circular orbit of the electron, and \( \delta z \) the shift along the direction of \( F \) between the electron and the nucleus induced by the external field. For small values of \( \delta z \) we may approximate the Coulomb force on the electron as \( \delta z / r^3 \), which balances the force exerted on the electron by \( F \) when

\[
F = \frac{\delta z}{r^3}.
\]  

(9)

The induced average dipole moment is \( d = \delta z \) and, from eq. (9) and the definition of \( \alpha \) (7),

\[
\alpha_{cl} = r^3 = n^6
\]

(10)
since for circular Bohr orbits \( r = n^2 \).

Even if this is a very simplified model, it was verified in [7] that it describes very accurately the classical system: the Hamilton’s equations for the electron were numerically solved in presence of the electric field. The electron energy was determined from its position and momentum. The numerical results were found to agree well with eq. (10) (see fig. 3 of [7]). It is therefore correct to assume that \( \alpha_{cl} \) is well approximated by eq. (10).

Eqns. (8) and (10) only agree for \( n \to \infty \); the greater discrepancies are for small \( ns \): for example, when \( n = 1 \) the ratio is \( \alpha_{cl} / \alpha_{QM} = 2/9 \approx 0.22 \).

3. - Improvements over the simple model

Both quantum and classical mechanics admit a remarkable unified description in terms of fluid dynamics: the Schrödinger equation

\[
i\hbar \frac{\partial \psi(r, t)}{\partial r} = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(r, t) \right) \psi(r, t)
\]

(11)

through the replacement

\[
\psi(r, t) = \sqrt{\rho(r, t)} \exp \left( \frac{i}{\hbar} S(r, t) \right)
\]

(12)

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may be rewritten into the set of two equations

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (13)
\]

\[
m \frac{d\mathbf{v}}{dt} = - \nabla U_{\text{eff}} \quad (14)
\]

where

\[
U_{\text{eff}} = U(r, t) - \frac{\hbar^2}{2m} \frac{\nabla^2 \sqrt{\rho}}{\sqrt{\rho}} = U(r, t) + U_q(r, t) \quad (15)
\]

\[
\mathbf{v}(r, t) = (\nabla S)/m \quad (16)
\]

The time evolution of a classical phase space distribution is given by the Liouville equation

\[
\frac{\partial f}{\partial t} = L(t) f \quad (17)
\]

\[
L(t) = \nabla_r U \cdot \nabla_p - \frac{\mathbf{p}}{m} \cdot \nabla_r \quad (18)
\]

from which, multiplying by 1 and \(\mathbf{p}\) respectively and then integrating,

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (19)
\]

\[
m \frac{d\mathbf{v}}{dt} = - \nabla_r U - \frac{1}{\rho} \nabla_r \Pi \quad (20)
\]

\[
\rho(r, t) = \int d\mathbf{p} f(r, \mathbf{p}, t) \quad (21)
\]

\[
\mathbf{v} = \frac{1}{m \rho} \int d\mathbf{p} \mathbf{p} f(r, \mathbf{p}, t) \quad (22)
\]

\[
\Pi_{ij} = \frac{1}{m} \int d\mathbf{p} p_i p_j f(r, \mathbf{p}, t) - \rho v_i v_j \quad (23)
\]

The only difference between the two sets of equations is that the role of the quantum potential \(U_q\) has been replaced by the stress tensor \(\Pi\).

From \(f\) one gets the projection over the position and momentum coordinates

\[
\rho(r, t) = \int d\mathbf{p} f(r, \mathbf{p}, t) \quad (24)
\]
\[
\bar{\rho}(\mathbf{p}, t) = \int d\mathbf{r} f(\mathbf{r}, \mathbf{p}, t) 
\]

(25)

In classical approximations the quantum dynamics of a system is computed through an averaging over an ensemble of classical trajectories. The average is done over the statistical distribution of initial conditions \( f \), with \( f \) chosen such as to closely reproduce the wave function in position or momentum space.

If \( f \) is to be stationary (as is the case here), it can depend only on constants of the motion [9]. A largely employed choice is to make \( f \) depending only upon the energy: \( f(\mathbf{r}, \mathbf{p}, t) \equiv f(E) \). There is not an unique choice possible for \( f \) since–classically–does not exist any \( f \) such that both \( \rho \) and \( \bar{\rho} \) are equal to their quantum mechanical counterpart. The choice is done on the basis of mathematical simplicity and accuracy.

Once a choice for \( f \)–and therefore for \( \rho, \bar{\rho} \)–is done, the calculations of the previous section still hold: simply, they are to be repeated for an ensemble of electrons, each of them is still obeying Newton’s equations, and in particular follows a circular orbit. Therefore, eq. (10) is replaced by its average

\[
\alpha = < r^3 > = \int d\mathbf{r} r^3 \rho(\mathbf{r}) .
\]

(26)

Notice that the model of [6, 7] may be seen as a particular case, by putting \( \rho \sim \delta(\mathbf{r}(t) - \mathbf{r}_K(t)), \bar{\rho} \sim \delta(\mathbf{p}(t) - \mathbf{p}_K(t)) \), with \( \mathbf{r}_K, \mathbf{p}_K \) position and momentum corresponding to a Kepler orbit.

I will consider three special cases:

1. first of all, the true quantum mechanical distribution is used for \( \rho \)

\[
\rho(\mathbf{r}) = |\psi_{nlm}(\mathbf{r})|^2
\]

(27)

with \( l = |m| = n - 1 \). This is an obvious choice, and is done in order to give an insight of the effectiveness of the method when applied under those which should be the conditions closest to the true ones. It has the defect that \( \rho \) now encompasses a region classically forbidden to the
electron: from

$$\frac{p^2}{2} - \frac{1}{r} = -\frac{1}{2n^2}$$

(28)

one gets \(r \leq 2n^2\).

2. The second choice is therefore to use a “truncated” distribution:

$$\rho = \begin{cases} 
C|\psi_{nlm}(r)|^2, & r < 2n^2 \\
0, & r \geq 2n^2 
\end{cases}$$

(29)

where \(C\) stands for a normalization constant.

3. Finally, I use a microcanonical distribution

$$f(E) = \frac{1}{8\pi^3} \delta \left( E + \frac{1}{2n^2} \right)$$

(30)

from which one obtains, after substitution in eq. (24),

$$\rho \propto \left( \frac{1}{r} - \frac{1}{2n^2} \right)^{1/2}$$

(31)

which is a real quantity only for \(r \leq 2n^2\). This microcanonical distribution is largely used in classical calculations of ion–hydrogen scattering processes for generating initial electron distributions, since it has the property of correctly reproducing the true electron momentum distribution \(\tilde{\rho}\).

All the integrals (26) may be performed analytically using the \(\rho_s\) of items 1-3. In table 1 I report the values for the polarizability obtained using 1–3, together with the values from eqns. (8) and (10). It is clearly discernible the slow convergence of \(\alpha_{cl}\) to \(\alpha_{QM}\) if compared, in particular, to \(\alpha_2\) which already at \(n = 1\) is within 20% of the true value. It is curious, on the other hand, the behaviour of \(\alpha_3\) which is always very close to \(\alpha_{QM}\) and, for \(n = 4, 5\) is the best approximation, but becomes worse at large \(ns\). Another point to remark is that, for large \(n\), \(\alpha_1\) and \(\alpha_2\) become nearly equal, as it should be from their definition. On the average, using any of the suggested distributions allows at least to halve the error with respect to the results of ref. [7].

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4. - Conclusions

In ref. [7] it is remarked that the main motivation of their work was to show that some quantal results may be recovered, at least partially, within a purely classical framework, provided only that the initial conditions be chosen as compatible as possible with the laws of quantum mechanics. This paper follows exactly that line of thought, being a refinement of that work in that the initial conditions have been chosen in a more correct manner, but still remaining within a classical description of the system. One may wonder if the price paid to have this greater accuracy is too high, since we used exact wave–functions, which is equivalent to solve the quantum mechanical problem. It is not so, since significant improvements are obtained using no matter which distribution, even that of eq. (31) which is based upon purely classical considerations. The other two distributions have been chosen just to provide the reader with a comparison. This is important for all these cases where extracting the wave function is too difficult and one is forced to resort to approximations. As already pointed out in [7], it could be worth exploring in some of such situations.

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This work has been supported by a grant of the Italian MURST. The hospitality offered by the Consorzio RFX is acknowledged.
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| n  | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\alpha_{cl}$ | $\alpha_{QM}$ |
|----|------------|------------|------------|---------------|---------------|
| 1  | 15/2       | 3.616      | 8/5        | 1             | 9/2           |
|    | (1.67)     | (0.80)     | (0.36)     | (0.22)        |               |
| 2  | 210        | 127.6      | 512/5      | 64            | 156           |
|    | (1.35)     | (0.82)     | (0.66)     | (0.41)        |               |
| 3  | 1701       | 1350.6     | 5832/5     | 729           | 1377          |
|    | (1.24)     | (0.98)     | (0.85)     | (0.53)        |               |
| 4  | 7920       | 7069.7     | 32768/5    | 4096          | 6720          |
|    | (1.18)     | (1.05)     | (0.98)     | (0.61)        |               |
| 5  | 53625/2    | 25313      | 25000      | 15625         | 46875/2       |
|    | (1.14)     | (1.08)     | (1.07)     | (0.67)        |               |
| 6  | 73710      | 71561      | 373248/5   | 46656         | 65772         |
|    | (1.12)     | (1.09)     | (1.13)     | (0.71)        |               |
| 10 | 1.328 $10^6$ | 1.325 $10^6$ | 1.6 $10^6$ | 1 $10^6$     | 1.2375 $10^6$ |
|    | (1.07)     | (1.07)     | (1.29)     | (0.81)        |               |

**Table 1**: Polarizability calculated from the different methods explained in the text. $\alpha_{1,2,3}$ from choices 1, 2, 3 respectively; $\alpha_{cl}$ from eq. (10); $\alpha_{QM}$ quantum mechanical value from eq. (8). Between parentheses are reported the ratios $\alpha/\alpha_{QM}$. $n$ is the principal quantum number.