Orbits of the hydrogen electron in a uniform electric field

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The linear Stark effect is investigated, using the old quantum theory and the equations of motion of the electron in orbital variables. In contrast to the well-known solution in terms of parabolic coordinates, the new form has a simple geometric interpretation, namely, perturbation by the uniform electric field leads in the first approximation to a slow regular precession of the electron orbit around the direction of the field (subject to a single additional condition). This geometric picture outwardly resembles electron orbits precessing around a uniform magnetic field in the normal Zeeman effect.

Atomic physics textbooks, especially chapters devoted to the old quantum theory, with their classical ideas on the trajectories of mass points, traditionally present two of the simplest examples of space quantization of electron orbits in the hydrogen atom placed in uniform electric or magnetic fields (linear Stark effect and normal Zeeman effect). This provides a clear demonstration of the quantization of perturbed energy levels of the atom and the corresponding picture of spectral-line splitting in simple cases.[1–4] Both problems are investigated by the methods of classical mechanics, but the approaches to them differ by the choice of the coordinate frame (based on the properties of the perturbing field), and the consequence of this is that the form of the solutions obtained for the electron orbit parameters is also different. In the case of the electric perturbing field, the parabolic coordinates, one of which is the equatorial angle measured from the direction of the field, is particularly suitable (because of the convenience of the separation of variables), whereas in the case of the perturbing magnetic field, the most suitable are spherical coordinates because they ensure the simplest transformation to orbital variables (and, as a consequence, to orbital quantum numbers) relative to moving coordinate axes that undergo, together with the plane of the perturbed orbit, a regular secular precession about the direction of the field.[1–4] This remarkable property of the solution of the second problem (which, in modern treatments, is a consequence of the general symmetry properties of the magnetic and rotation fields) has led, firstly, to an exceptionally simple and clear geometric interpretation of the perturbed motion of the electron in terms of the familiar terminology of orbital mechanics and, secondly, it enables us to use (by virtue of the adiabatic principle) the usual quantization scheme for elliptic orbits in precessing coordinate planes when we estimate the electron level shifts. On the other hand, the first problem is not amenable to a comparably simple interpretation despite its mathematical convenience. It leads only to general conclusions about the nature of the perturbed orbit between certain particular limits.[1]

In their classical form, both problems are, of course, part of history (although they are still of pedagogic value to students of atomic physics). From purely methodological and general points of view, it is natural to try to examine both problems in terms of orbital variables because it may then be possible to compare and contrast the solutions thus obtained with known solutions.

Our interest in this topic has been stimulated by a paper by one of the present authors[5] ('Evolution of a satellite orbit under the influence of a small perturbing force that is constant in magnitude and direction') in which a basically similar problem in celestial mechanics was examined in terms of orbital variables. The point is that the general solution of this problem includes two exceedingly simple special solutions (that are of direct interest here) in which, when certain initial conditions are satisfied, the perturbed orbit of the satellite (and, in our case, that of the electron) retains its form in the first approximation (i.e., to within secular perturbations of the second order of small quantities) and executes a regular secular precession around the direction of the perturbing field (in our case, the electric field). We have thus established an interesting fact: the orbit of a hydrogen electron in a uniform electric field behaves outwardly (i.e., in the geometric picture) in the same way as in the normal Zeeman effect (but with certain differences). We have also found that, when these remarkable solutions are applied to the quantization of perturbed allowed electron orbits on the basis of the adiabatic principle (i.e., by analogy with Ref. 1 and other references in the case of the normal Zeeman effect), we are led to an unexpected and useful result, namely, that the quantization and selection rules for the equatorial quantum number n_ψ relative to the precessing orbital axes are somewhat different from the usual rules relative to fixed coordinate axes (this is explained below in greater detail). This fact (established by comparing the new form of the solution with 'standard', i.e., existing, solutions) has in its turn taken us back to the second problem (in which the 'old' quantization and selection rules for n_ψ are used relative to the precessing axes), which has led us to a still more unexpected result: both in Sommerfeld's[1] and in many other textbooks that discuss the old theory of the normal Zeeman effect, the expression for the change in the total energy of the electron does not for some reason take into account the potential energy of the interaction between the magnetic moment of the atom and the perturbing magnetic field (which is undoubtedly taken into account when this problem is examined in wave mechanics). When this inaccuracy is removed, we are led to the 'modern' rule for the quantization

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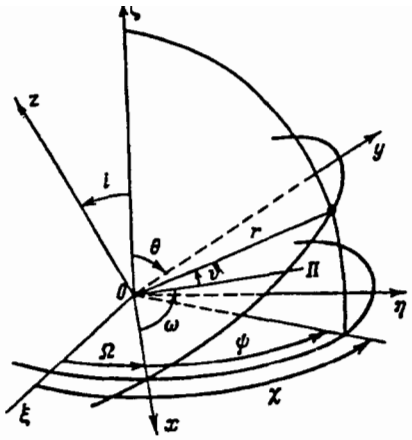

FIG. 1. Coordinate frames and orbital variables.

of the equatorial quantum number relative to the precessing axes that was 'discovered' in the first problem.

Thus, by comparing two different forms of the solution for a simple special case we are led to a modified quantization rule for the equatorial quantum number relative to moving coordinate axes that precess about a special direction (e.g., in spatial problems in which the adiabatic principle is employed). This conclusion may appeal to physics teachers and to others interested in atomic physics and its history (it may give rise to discussions that would also be exceedingly interesting).

1. Let us therefore consider (in the nonrelativistic formulation) the motion of an electron as a mass point in the central-force field of the nucleus in the hydrogen atom (or the nucleus of a hydrogen-like atom of charge Ze) in the presence of a perturbing acceleration $\mathbf{f}=(-Ee/m_0)\vec{\zeta}_0$ which is constant in magnitude and direction and is due to a uniform electric field E (e, m_0 are the electric charge and the rest mass of the electron and $\vec{\zeta}_0$ is a unit vector in the direction of the $O\zeta$ axis of an inertial Cartesian set of coordinates $O\xi\eta\zeta$ with origin at the center of the nucleus; see Fig. 1). If, by analogy with Ref. 5, we take the small parameter ε of this problem to be the ratio $|\vec{\mathbf{f}}|/f_k$ where f_k is the acceleration due to the Coulomb force of attraction between the electron and the nucleus at a distance equal to the orbital semiaxis $a(\varepsilon=Ea^2/Ze)$, then it follows from the general solution of the analogous problem in celestial mechanics[5] that, in the first approximation (i.e., to within second-order secular perturbations in the parameter ε), the eccentricity e_o, the focal parameter p, the inclination i, and the angular separation ω between the pericenter and the node (see Fig. 1) will in this case execute synchronous long-period oscillations (with period corresponding to the number of revolutions of the electron, of the order of $1/\varepsilon$) for which the semimajor axis of the orbit, $2a$, remains constant and the plane of orbit executes slow monotonic precession (in the angle Ω; see Fig. 1) about the direction of the perturbing field (the $O\zeta$-axis).[1)] However, the most interesting of this family of solutions are the two special 'quasistatic' solutions, corresponding to the initial conditions $\sin i_0=e_o$, $\omega_0=\pm 90°$ for which the parameters i, e_o, ω, and the semimajor axis of the orbit subsequently remain constant, i.e.,

$$\sin i=\varepsilon_o\equiv\varepsilon_0=\sin i_0,\qquad \omega\equiv\omega_0=\pm 90°, \tag{1.1}$$

and the plane of the orbit executes regular precession around the ζ-axis with constant mean (over the period T_1 of one revolution in orbit) angular velocity $d\Omega/dt=\pm(3/2)(\varepsilon/T_1)\,\mathrm{sign}(\cos i_0)$ or, when the parameters of the electron are taken in the Gaussian system of the units,

$$d\Omega/dt=\pm(3/2)E(a/m_0Z)^{1/2}\,\mathrm{sign}\cos i_0, \tag{1.2}$$

in which the signs $\pm$ correspond to initial values $\omega_0=\pm 90°$.

These quasistationary orbits outwardly resemble analogous perturbed orbits in the normal Zeeman effect, but with the fundamental difference that here the eccentricity and the inclination are not independent of one another (they are related by $e_o=\sin i$) and, in addition, the precession angular velocity of the orbit depends on its semimajor axis a (in the normal Zeeman effect it is the same for all orbits[1-4]).

2. The solutions given by (1.1) and (1.2) enable us to calculate in a simple elementary manner the shifts of the total energy levels of an electron. This is based on the adiabatic principle and on the analogy with the usual procedure adopted in treatments of the normal Zeeman effect in the old quantum theory.[1-3]

Let us therefore introduce moving coordinate frames that precess around the ζ-axis of the fixed frame $O\xi\eta\zeta$ together with the allowed orbits in the family (1.1), (1.2), so that the equatorial angular coordinates of the electron (χ in the fixed system, ψ in the moving system) are related by $\chi=\psi+\Omega$ (Fig. 1). We can now set up in the usual way the expressions for the kinetic energy T of the electron in the absence of the electric field [$T(r,\theta,\dot{r},\dot{\theta},\dot{\psi})$ or $T(0)$] and in the presence of the field [$T(r,\theta,\dot{r},\dot{\theta},\dot{\chi})$ or $T(E)$], so that, to within second-order terms in $d\Omega/dt$, we have

$$\Delta T=T(E)-T(0)=p_\psi d\Omega/dt, \tag{2.1}$$

where p_ψ is the electron momentum corresponding to the coordinate ψ in the precessing frame. If we use (1.2) for $d\Omega/dt$, and also the quantization conditions for the momentum p_ψ and the semimajor axis a of the orbits [$p_\psi=(h/2\pi)n_\psi$, $a=h^2n^2/4\pi^2m_0Ze^2$, where n and n_ψ are the principal and equatorial quantum numbers and h is the Planck constant), we obtain [according to (2.1)], the following expression for the change in the kinetic energy:

$$\Delta T=\pm 3h^2En|n_\psi|(8\pi^2m_0Ze)^{-1}, \tag{2.2}$$

where the signs $\pm$ correspond to the initial values $\omega_0=+90°$ and $\omega_0=-90°$.

The change in the potential energy of the electron, ΔV, can be calculated either by taking a time average of the expression $\Delta V=Ee\zeta$ (over an interval corresponding to one revolution of the electron in orbit) and using the equations of perturbed motion. Alternatively, and this is sim-

pler but gives the same result, it can be found by evaluating the scalar product $\Delta V=-\mathbf{E}\cdot\mathbf{P}$ of the electric field $\mathbf{E}$ and the electric dipole moment $\mathbf{P}$ whose magnitude is[1] $(3/2)ee_0a$ and whose direction lies along the line drawn from the 'center of gravity' of the electron in its elliptic orbit and the nucleus. Since $\sin^2 i=e_0^2=1-(m_\varphi/n)^2=1-\cos^2 i=1-(n_\psi/n_\varphi)^2$ and since, as a consequence, $n_\varphi^2=n|n_\psi|$ (n_φ is the azimuthal quantum number), we finally obtain

$$\Delta V=\mp 3h^2En(n-|n_\psi|)(8\pi^2m_0Ze)^{-1}, \qquad (2.3)$$

where the sign of the increase is opposite to that of the initial value of ω_0.

We note particularly the case of the circular orbit ($e_0=0$, $i_0=0$ or $i_0=180°$) which is stable[5] against the perturbing field and in the first approximation (i.e., to within the second-order secular perturbations) does not change its energy ($\Delta T=\Delta V=0$; see also Ref. 2). We also note that it is only in this case that the equatorial quantum number reaches is maximum numerical value $|n_\psi|=n$.

Thus, when (2.2) and (2.3) are taken into account and $e_0=0$, the change in the total energy of the electron is given by

$$\Delta W=\pm 3h^2n(n-2|n_\psi|)(8\pi^2m_0Ze)^{-1} \quad \text{for } |n_\psi|<n,$$
$$=0 \quad \text{for } |n_\psi|=n, \qquad (2.4)$$

where the positive sign corresponds to the case where the geometric center of the elliptical orbit lies above the equatorial plane $O\xi\eta(\omega_0=-90°)$ and the negative sign corresponds to the situation where it lies below this plane ($\omega_0=+90°$; see Fig. 1).

3. If we now try to use (2.4) to calculate the frequency shift $\Delta\nu$ for the Balmer lines of hydrogen [$\Delta\nu=(\Delta W_1-\Delta W_2)/h$], using only integral values of $|n_\psi|$ and the traditional rules for quantum transitions ($\Delta n_\psi=0$ for the π-components and $\Delta n_\psi=\pm 1$ for the σ-components), we find that the results do not agree with the classical picture of line splitting.[1-3] Complete agreement is achieved only if we use in (2.4) both integral and half-integral values of $n_\psi(1/2\leqslant|n_\psi|\leqslant n)$ and also modify the selection rules for n_ψ:

$$\Delta|n_\psi|=0 \text{ for } \pi\text{-components},$$
$$\Delta|n_\psi=\pm 1/2 \text{ for } \sigma\text{-components}. \qquad (2.5)$$

As an illustration, Tables I and II list values of the frequency shift Δ for the Balmer line H_α, calculated in accordance with these rules in units of the constant $A=3hE/8\pi^2m_0e$ (the asterisk marks the value $\Delta W_2=0$ that corresponds to a circular orbit in the $n=2$ final state).

As can be seen, these data agree completely with existing results[1] (this also applies to the H_β line). It is interesting that, beginning with the H_γ line, the selection rules given by (2.5) must be extended, i.e., the $\Delta|n_\psi|=0$ transitions for the π-components must be augmented by $\Delta|n_\psi|=\pm 1,\pm 2,...,\pm[(|n_1-n_2|-1)/2]$, transitions and the $\Delta|n_\psi|=\pm 1/2$ transitions for the σ-components must be augmented by $\Delta|n_\psi|=\pm 3/2,\pm 5/2,...,\pm([(|n_1-n_2|-1)/2]+1/2)$ transitions. We thus see that the 'missing' π-components of H_γ with $\Delta=\pm 2$ and the π-components of H_δ with $\Delta=0,\pm 4,\pm 8$ appear for $\Delta|n_\psi|=1$, whereas σ-components of H_δ with $\Delta=\pm 1/2$ that are 'missing' for $\Delta|n_\psi|=\pm 1/2$ appear for $\Delta|n_\psi|=3/2$ (no new splittings occur under these conditions).

TABLE I. π-components of H_α ($n_1=3, n_2=2$).

$\lvert n_{\psi 1}\rvert \to \lvert n_{\psi 2}\rvert$	$\pm 3(3-2\lvert n_{\psi 1}\rvert)$	$\pm 2(2-2\lvert n_{\psi 2}\rvert)$	Δ
$1/2 \to 1/2$	± 6	± 2	$\pm 4, \pm 8$
$1 \to 1$	± 3	0	± 3
$3/2 \to 3/2$	0	∓ 2	± 2
$2 \to 2$	∓ 3	0*	∓ 3

TABLE II. σ-components of H_α.

$\lvert n_{\psi 1}\rvert \to \lvert n_{\psi 2}\rvert$	$\pm 3(3-2\lvert n_{\psi 1}\rvert)$	$\pm 2(2-2\lvert n_{\psi 2}\rvert)$	Δ
$1/2 \to 1$	± 6	0	± 6
$1 \to 1/2$	± 3	± 2	$\pm 1, \pm 5$
$1 \to 3/2$	± 3	∓ 2	$\pm 5, \pm 1$
$3/2 \to 1$	0	0	0
$3/2 \to 2$	0	0*	0
$2 \to 3/2$	∓ 3	∓ 2	$\mp 1, \mp 5$
$5/2 \to 2$	∓ 6	0*	∓ 6

4. Our investigation and the comparativie analysis of the two alternative approaches to the solution of this particular problem have enabled us to establish a fundamentally important fact: if we use moving coordinate axes with an additional degree of freedom relative to a given direction (precession angle ψ) in problems involving space quantization, we find that, in general, this involves additional half-integral quantization of the equatorial quantum number n_ψ and a corresponding modification of the selection rules (in general, $\Delta n_\psi=0\pm 1,\pm 2,...$ for the π-components and $\Delta n_\psi=\pm 1/2,\pm 3/2,...$ for the σ-components of the spectral lines). On the other hand, it is well-known that the normal Zeeman effect is discussed in the old quantum theory relative to moving coordinate axes that precess about the direction of a uniform magnetic field. This involves the usual quantization and selection rules for the quantum number n_ψ, which is in clear conflict with the fact established above. By re-examining this classical problem we found one further significant error that has crept into the publications quoted above[1-8] and elsewhere in the literature when the expression for the change in the total energy of the electron is established. For some reason, the potential energy of the interaction between the magnetic moment of the atom and the perturbing uniform magnetic field is ignored (this energy is numerically equal to the increase in the kinetic energy, ΔT, due to the precession of the orbital plane of the electron, $\Delta T=hn_\psi eH/4\pi m_0c$ where H is the magnetic field[1-3]). When this error is corrected, the increase in the total energy, ΔW, of the electron becomes greater by a factor of two, in which case the application of the new quantization

and selection rules for the equatorial quantum number relative to precessing axes reproduces the classical picture of spectral line splitting ($\Delta\nu=0$ for π-components, $\Delta\nu=IeH/4\pi m_0 c$ for σ-components). This is a further demonstration of the validity of the conclusions drawn above.[2)]

[1)]The evolution of an orbit is investigated in Ref. 5 interms of the equations of celestial mechanics averaged over the interval 0, 2π with the independent variable taken to be the angular separation v measured in the plane of the unfolding orbit of a mass point and given by the expression $dv/dt=k^{1/2}p^{-3/2}(1+\varepsilon_o\cos\vartheta)^2$, where t is the running time, k is the product of the gravitational constant and the mass of the central attracting body (in the case of an electron $k=Ze^2/m_0$, $p=a(1-e_o^2)$ is the focal parameter of the orbit, and ϑ is the true anomaly). The use of this variable enables us to treat motion in the central force field as rolling of the orbital plane (with the angle ϑ measured from a fixed line) on a conical surface traced out by the position vector of the mass point with origin at the center of attraction O.

[2)]It is interesting to note that if we apply the above 'extended' selection rule to the normal Zeeman effect ($\Delta|n_\psi|=0,\pm1,\pm2,\ldots,\pm\max(n_1,n_2)$ for the π-components and $\Delta|n_\psi|=\pm1/2,\pm3/2,\ldots,\pm(\max(n_1,n_2)-1/2)$ for the σ-components, then we have the theoretical possibility of a wider picture of line splitting: for example, for the H_α line we have (in units of the constant $\Delta_H=heH/4\pi m_0 c$), $\Delta_H=\{0,\pm2,\pm4\}$ for the π-components and $\Delta_H=\{\pm1,\pm3,\pm5\}$ for the σ-components. The number of splittings increases by unity (in the same step of ±2) for each subsequent line.

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