c. A weak electric field - the classical Stark effect

As we saw in our discussion of the Kepler problem, the orbit is fixed in space due to the constant of the motion, $A$, the Lenz vector. The fact that this constant is a vector that points along the semi-major axis assures us that the orbit is fixed in space. As for any central potential problem, the angular momentum, $L$, also a vector, is conserved. Conservation of $L$ assures us that the motion takes place in a plane that is perpendicular to the plane of the orbit. Imposition of the electric field destroys the spatial symmetry that causes $L$ to be conserved so the motion is no longer constrained to a plane. If this field is weak then the orbit will resemble an ellipse, but the orbital plane and shape do not remain constant. To simplify the problem we note that under these circumstances the electron moves around the nearly elliptical orbit in a time short compared with the time required for changes in the plane and shape of the trajectory. Thus, the time dependencies of the shape and orientation of the orbit provide a classical picture of the hydrogen atom subjected to a weak constant electric field.

Before examining these time dependencies we return to the permanent electric dipole moment associated with a given excited state of hydrogen. What is the classical correspondence with this permanent dipole moment? What is its magnitude? To answer these questions we consider a classical hydrogen atom, an electron executing a Keplerian orbit about a proton as shown in the figure. We know from Kepler's second law, the law of equal areas, that the areas swept out in equal times are equal as depicted in the figure. Therefore, the electron's velocity at pericenter is greater than at apocenter so the average time spent near these orbital positions differ. In fact, it is easy to see that because of these differences, the electron spends more time near apocenter than near pericenter so the time average of the electron's charge is asymmetric. This, together with symmetry about the major axis, leads to a permanent electric dipole moment pointing in the direction of $A$.

![Diagram](https://via.placeholder.com/150)

The magnitude of this moment can be obtained by calculating the time average of the position along the major axis. In plane polar coordinates and atomic units this is given by
Using the equation of the orbit and the relationship between angular momentum, energy and eccentricity,

\[ \epsilon = \sqrt{1 - \frac{\ell^2}{n^2}} \]

the magnitude of the dipole moment for a given orbit that is characterized by its energy \( n \) and its angular momentum \( \ell \) is

\[ \langle p \rangle = -\left(\frac{3}{2}\right)n^2A \]

so that the energy shift caused by the external electric field \( \mathbf{F} \), \(-\mathbf{p} \cdot \mathbf{F}\), is given by

\[ \Delta E = -\left(\frac{3}{2}\right)n^2A \frac{\ell}{2} \mathbf{F} \]

Note that the greater the energy of the orbital state, the greater the dipole moment and thus the energy shift. It is important that the appearance of \( n \) and \( \ell \) in the derivation in no way signifies that this is a quantum mechanical result. These quantities are merely the classical energy and angular momentum in atomic units. Both are of course considered to be continuously variable. The accompanying table is a listing of some pertinent Keplerian quantities in atomic units.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>( E = -1/2n^2 )</td>
</tr>
<tr>
<td>Semi-major axis</td>
<td>( a = n^2 )</td>
</tr>
<tr>
<td>Semi-minor axis</td>
<td>( b = n\ell )</td>
</tr>
<tr>
<td>Orbital frequency</td>
<td>( \omega_n = 1/n^3 )</td>
</tr>
<tr>
<td>Orbital period</td>
<td>( \tau = 2\pi a^{3/2} = 2\pi n^3 )</td>
</tr>
<tr>
<td>Orbital eccentricity</td>
<td>( \epsilon = [1 - (\ell/n)^2]^{1/2} =</td>
</tr>
<tr>
<td>Pericenter (from focus)</td>
<td>( r_{\text{min}} = n^2(1 - \epsilon) = \ell^2/(1 + \epsilon) )</td>
</tr>
<tr>
<td>Apocenter (from focus)</td>
<td>( r_{\text{max}} = n^2(1 + \epsilon) = \ell^2/(1 - \epsilon) )</td>
</tr>
</tbody>
</table>
Previously, we found that the quantum mechanical value of $A_z$ is

$$A_z = \frac{n_1 - n_2}{n}$$

so that the energy shift is

$$\Delta E = \frac{3}{2} n (n_1 - n_2) F$$

which is identical to $E^{(1)}_n$, the quantum mechanical result.

We return now to the time dependence of the orbital motion and emphasize that because the electronic motion is fast with respect to changes in the shape of the orbit we may consider the orbit as the dynamical entity. The time dependence of $L$ can be obtained by using the classical relationship for the torque on an electric dipole

$$\text{Torque} = \dot{L} = p \times F = \left(\frac{3}{2}\right)n^2 [A \times F]$$

Again, the appearance of $n$ does not signify a quantal result. We can, however, see that, since $F$ is in the z-direction, $\dot{L}_z = 0$ and $L_z$ is a constant of the motion.

There is considerably more algebra involved in obtaining the equation for $A$ so we shall not do this derivation here. The reader is referred to the original paper referenced at the beginning of this section. The result is

$$\dot{A} = \left(\frac{3}{2}\right)[L \times F]$$

Notice that, again since $F$ is in the z-direction, $\dot{A}_z = 0$ so $A_z$ is a constant of the motion. That both $L_z$ and $A_z$ are constants of the classical motion indicates that their quantum mechanical operators will commute with the hamiltonian, thus permitting the problem of a hydrogen atom in an electric field, the Stark effect, to be separated in some coordinate system, in this case parabolic coordinates.
The coupled symmetric equations for $\hat{A}$ and $\hat{L}$ can easily be uncoupled by differentiating one and substituting into the other. For example, the equation of motion for $\hat{A}$ is given by

$$\ddot{A} = -\left(\frac{3}{2}n\right)^2 [A(F \cdot F) - F(F \cdot A)]$$

from which it is immediately seen that $\ddot{A}_z = 0$, as it must since $A_z$ is a constant of the motion. The $x$- and $y$-components of $\hat{A}$ are given by

$$\ddot{A}_i(t) = -\left(\frac{3}{2}nF\right)^2 A_i(t)$$

from which, taking $Ay(t = 0) = 0$, we obtain

$$A_x(t)^2 + A_y(t)^2 = A_{x0}^2 \cos^2(\omega_S t) + A_{y0}^2 \sin^2(\omega_S t)$$

where $A_{i0}$ are the values of the $x$- and $y$-components respectively at $t = 0$ and $\omega_S = (3/2)nF$, the Stark frequency. These relationships for the components of $A$ show that the Lenz vector describes an ellipse in a plane perpendicular to the direction of the applied field and that the frequency of the motion is $\omega_S$.

Although the motion of $A$ indicates that the shape of the elliptical orbit is changing, this change can be associated with changes of only the minor axis because the energy remains constant and the energy is given by $a$, the semi-major axis.

If the equations of motion for $A$ and $L$ are uncoupled to give an equation that describes the motion of $L$ it is found that it also outlines an ellipse with frequency $\omega_S$, but in a plane perpendicular to the $z$-axis $a$. The figure below shows the orbit and the motion of the vectors $A$ and $L$. Clearly, these vectors and orbit revolve rigidly about the field direction since $A$ and $L$ are always in the plane and perpendicular to the plane of the orbit respectively. The entire assembly rotates with frequency $\omega_S = (3/2)nF$, the Stark frequency.
Our classical view of the Stark effect on hydrogen atoms is one of a pulsating ellipse, rotating about the electric field vector. The pulsation causes the semi-minor, but not the semi-major axis to change as the plane of the orbit rotates. The figure below shows the trajectory of the electron in a classical hydrogen atom having $n = 11$, $m = 1$ and $k = 4$ that is subjected to an external electric field, $F$. The trajectory was generated by numerical solution of Hamilton's equations of motion with $|F| = 2.917 \times 10^{-7}$ a. u. (1500 V/cm). The nearly Keplerian orbits of the electron are slightly distorted and rotate around the electric field vector as described above.

Before leaving the subject of the classical hydrogen atom we recall the expression for the energy obtained in the quantum mechanical solution.

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\[ E_n^{(1)} = \frac{3}{2} n (n_1 - n_2) F \]

Now, the difference \((n_1 - n_2)\) changes by 2 for fixed \(m\) because the quantum numbers are related by

\[ n = n_1 + n_2 + |m| + 1 \]

so that the difference in energy between adjacent levels of the same \(m\) is given by

\[ \Delta E = \frac{3}{2} n (2) F = 3nF \]

If, however, adjacent values of \(m\) are considered as shown in the figure, then the separation between adjacent Stark levels is

\[ \Delta E = \frac{3}{2} n F = \omega_S \]

the Stark frequency.

This is not an accident! According to the correspondence principle, radiation given off when a system undergoes a transition between levels separated by energy \(E\) is \(E/\hbar\), which, in our case is precisely \(\omega_S\). The frequency of revolution of the orbit about \(F\) is always \(\omega_S\). The energy changes because it is the product of the \(z\)-component of the electric dipole moment and the magnitude of the field. Therefore, in our classical picture, different energy levels correspond to different orientations of the orbital plane with respect to the external field. Since the frequency of
revolution remains constant, the energy levels at any given value of \( F \), a vertical line in the above figure, have constant separation.

For further details, see: