b. A weak electric field - the quantum mechanical Stark effect

If a hydrogen atom is immersed in a weak electric field in the z-direction \( \mathbf{E} = F \hat{k} \), the interaction energy is simply

\[
H_S = -p \cdot \mathbf{E} = e r \cdot \mathbf{E} = eFz
\]

where \( p \) is the electric dipole moment of the hydrogen atom. The unperturbed Hamiltonian, i.e. when \( \mathbf{E} = 0 \) is the usual Coulomb Hamiltonian

\[
H_0 = H_{\text{Coulomb}} = \frac{p^2}{2m} - \frac{e^2}{r}
\]

The eigenstates of \( H_0 \) are the hydrogen atom wave functions \( |n\ell m\rangle \). The correction to the energy resulting from application of the electric field is

\[
E_S^{(1)}(1) = H_S = eF<n\ell m,z|n\ell m,z>
\]

For the ground state the first order correction is given by

\[
E_{n=1}^{(1)} = eF<100|z|100> = 0
\]

which vanishes because the nondegenerate ground state has definite parity, \( \ell = 0 \), so that the integral above is odd. This is another way of saying that because the ground state is non-degenerate, the spherical and parabolic eigenfunctions for the ground state of hydrogen are the same.

To find the effect of the field on the ground state we must use second order perturbation theory, which in this case gives

\[
E_{n=1}^{(2)} = \sum_{n \neq 1, \ell, m} \frac{e^2F^2}{E_{n=1}^{(0)} - E_{n}^{(0)}} |<n\ell m,z|100>|^2
\]

This sum can be evaluated exactly [Dalgarno and Lewis, Proc. R. Soc. (London), A233, 70 (1956) and C. Schwartz, Ann. Phys. (NY), 6, 156, 170, 178 (1959), see also Berkowitz]. The answer is
\[ E_{n=1}^{(2)} = -\frac{9}{4} a_o^3 F^2 \]

where \( a_o \) is the Bohr radius. Notice that \( E_{n=1}^{(2)} \propto F^2 \). In general, if there is no permanent electric dipole moment, a moment may be induced by the field. The relationship is linear so that

\[ \mu_{\text{induced}} = \alpha F \]

where, in this context, \( \alpha \) is the dipole polarizability, not the fine-structure constant and \( \mu \) represents an electric dipole moment. Therefore, in weak fields, for atoms without permanent electric dipole moments, the first order Stark effect vanishes. To see the effect of the weak electric field the second order effect must be computed, as is the case for hydrogen in the ground state.

Now, how about excited states? As we have seen previously, as a result of the accidental degeneracy, excited states of hydrogen may have permanent dipole moments. We therefore expect to observe the linear Stark effect because, from elementary physics, the energy of a permanent electric dipole in an electric field is given by

\[ E = -\mu_{\text{permanent}} \cdot F \]

Indeed, the linear Stark effect is observed for excited states of hydrogen.

To find the first order Stark shift in excited hydrogen we first consider \( n = 2 \). There are 4 degenerate unperturbed states so we must use degenerate perturbation theory. The matrix representation of \( H_S \) will be a \( 4 \times 4 \) matrix

\[
\begin{pmatrix}
<200|H_S|200> & <200|H_S|210> & <200|H_S|211> & <200|H_S|21-1>\\
<210|H_S|200> & <210|H_S|210> & <210|H_S|211> & <210|H_S|21-1>\\
<211|H_S|200> & <211|H_S|210> & <211|H_S|211> & <211|H_S|21-1>\\
<21-1|H_S|200> & <21-1|H_S|210> & <21-1|H_S|211> & <21-1|H_S|21-1>
\end{pmatrix}
\]

We must find a basis set, linear combinations of the \( |n\ell m_\ell \rangle \), that diagonalizes this matrix. In general, this is difficult to do. In this case, however, symmetry considerations eliminate most of the matrix elements. We note that

1. All diagonal elements vanish as in the ground state (parity).
2. Parity depends only on $\ell$, not $m\ell$. Therefore, all matrix elements having the same value of $\ell$ vanish.
3. The only possible non-zero matrix elements are the off-diagonal elements in the first row and first column.
4. $[H_S, L_z] = 0$ since $H_S \propto z$ and $L_z$ contains only $\partial/\partial x$ and $\partial/\partial y$.

Now, since the basis kets for the matrix are eigenkets of $L_z$, we may write an off-diagonal element for which the values of $\ell$ are different as

$$
<n\ell' m'|z|n\ell m\ell> = <n\ell' m'| \left( \frac{L_z}{m\ell \hbar} \right) z|n\ell m\ell> \\
= \left( \frac{1}{m\ell' \hbar} \right) <n\ell' m'|z L_z|n\ell m\ell> \\
= \left( \frac{1}{m\ell' \hbar} \right) <n\ell' m'|z \left( L_z \right)|n\ell m\ell> \\
= \left( \frac{m\ell' \hbar}{m\ell \hbar} \right) <n\ell' m'|z|n\ell m\ell>
$$

from which we see that

$$(m\ell' - m) \hbar <n\ell' m'|z|n\ell m> = 0$$

so that

$$<n\ell' m'|z|n\ell m> = 0 \quad \text{if} \quad m\ell \neq m\ell'$$

There is therefore only one matrix element that we must evaluate because

$$<200|H_S|210> = <200|H_S|210> \equiv H_{S2}$$

evaluation of which is straightforward.
\[ H_{S2} = eF \int_0^\infty drr^2 \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi R_{20}^*(r) Y_{00}^*(\theta, \phi)(r \cos \theta) R_{21}(r) Y_{10}(\theta, \phi) \]

\[ = -3eFa_o \]

\[ = -Q \]

The eigenvalue problem thus becomes

\[
\begin{pmatrix}
0 & -Q & 0 & 0 \\
-Q & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
= E_2^{(1)}
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
\]

which we can solve using straightforward matrix multiplication. Noting that the constant \( E_2^{(1)} \) represents the unit matrix multiplied by \( E_2^{(1)} \), we have

\[
\begin{pmatrix}
0 & -Q & 0 & 0 \\
-Q & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
= E_2^{(1)}
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
\]

which becomes

\[
\begin{pmatrix}
-E_2^{(1)} & -Q & 0 & 0 \\
-Q & -E_2^{(1)} & 0 & 0 \\
0 & 0 & -E_2^{(1)} & 0 \\
0 & 0 & 0 & -E_2^{(1)}
\end{pmatrix}
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
= 0
\]

Setting the determinant of the coefficients of these four simultaneous homogeneous equations equal to zero yields
where, for convenience, we have let $E_2 = E_2^{(1)}$. Solution of this equation yields

$$E_2 = 0, 0, Q, -Q$$

Note that $E_2$ is linear in $F$ as suspected. Since the energy is given by $p_z F$, the $z$-components of the permanent dipole moments of these states are $0, 0, \pm 3e F a_o$.

We may find the eigenkets that diagonalize $H_S$ for $E_2 = 0$ by returning to the matrix equations. We have

$$
\begin{pmatrix}
0 & -Q & 0 & 0 \\
-Q & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
= 0
\begin{pmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{pmatrix}
$$

so that

$$
-C_2 Q = 0 \Rightarrow C_2 = 0 \\
-C_1 Q = 0 \Rightarrow C_1 = 0
$$

Therefore, $C_3$ and $C_4$ need not be zero and we have two of the unperturbed eigenkets reclaimed, namely $|211\rangle$ and $|21-1\rangle$. Recall that we chose the matrix representation such that $H_S$ is given by
\[
\begin{pmatrix}
<200|H_S|200> & <200|H_S|210> & <200|H_S|211> & <200|H_S|21-1>

<210|H_S|200> & <210|H_S|210> & <210|H_S|211> & <210|H_S|21-1>

<211|H_S|200> & <211|H_S|210> & <211|H_S|211> & <211|H_S|21-1>

<21-1|H_S|200> & <21-1|H_S|210> & <21-1|H_S|211> & <21-1|H_S|21-1>
\end{pmatrix}
\]

Notice that, since \([H_S, L_z] = 0\), i.e. \(m_\ell\) is a good quantum number, only states having the same values of \(m_\ell\) are mixed, that is, the ones for which \(C_1\) and \(C_2\) are the coefficients. This can be seen from the equation that we derived

\[
(m_\ell' - m)\hbar <n\ell'm'|z|n\ell'm> = 0
\]

because the matrix element must vanish unless \(m_\ell' = m_\ell\). To solve for the remaining eigenkets we put the next two eigenvalues back into the eigenvalue equation. For \(E_2^{(-)} = +Q\), we get

\[
-QC_2 = QC_1 \quad \& \quad -QC_1 = QC_2 \quad \Rightarrow \quad C_1 = -C_2
\]

so that

\[
|\psi_+\rangle = \frac{1}{\sqrt{2}} |210\rangle - \frac{1}{\sqrt{2}} |200\rangle
\]

Repeating this procedure yields \(|\psi_-\rangle\)

\[
|\psi_+\rangle = \frac{1}{\sqrt{2}} |210\rangle + \frac{1}{\sqrt{2}} |200\rangle
\]

The degeneracy is thus only partially removed by application of the field. The energy levels, under the influence of the weak electric field of magnitude \(F\) become
Although the asymmetry of the problem that results from having established a direction in space with the electric field makes it impossible to separate the Schrödinger equation in spherical coordinates, it still separates in parabolic coordinates. To first order the energy in atomic units is (see Bethe & Salpeter)

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

where the first term is the zero field energy. The parabolic quantum numbers are the same as those already obtained for the field-free solution. They are related by

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

It is convenient to define another parabolic quantum number. Of course, it is dependent upon the quantum numbers that arise naturally from the solution to Schrödinger's equation in parabolic coordinates. We define

\[ k = n_1 - n_2 = "electric quantum number" \]

Because of the constraints on \( n_1 \) and \( n_2 \), \( k \) changes in steps of 2 for fixed \( m \). In terms of the quantum number \( k \) the Stark energy is

\[ E_n^{(1)} = \frac{3}{2}nkF \]

so that, comparing with the expression for the energy of an electric dipole in a field

\[ E = -p_zF \]

we see that the z-component of the permanent electric dipole moment of a hydrogen atom in a weak field is
\[ p_z = \frac{3}{2} n k = \frac{3}{2} n (n_1 - n_2) \]

We know that the linear combinations of orbital states that we obtained by diagonalizing the Stark Hamiltonian for \( n = 2 \) are parabolic eigenfunctions. Therefore, we may obtain their parabolic quantum numbers by comparing the eigenenergies with the energy obtained in parabolic coordinates. That is, the energies

\[ E_2^{(1)} = 0, 0, \pm 3 e_a F = 0, 0, \pm 3 F \quad \text{(in au)} \]

must be in the form

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

with, of course, \( n = 2 \). The following table lists these quantum numbers and the values of \( p_z \) for each state \( n = 2 \).

<table>
<thead>
<tr>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>( m )</th>
<th>( k )</th>
<th>( \frac{3}{2} n k F ) (au)</th>
<th>( p_z ) (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>+3F</td>
<td>+3</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>-3F</td>
<td>-3</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

That the parabolic eigenfunctions can be expanded on the set of orbital eigenfunctions is no surprise. The set of eigenfunctions of a hermitian operator are always complete and form a basis set. Therefore, each set of eigenfunctions can be expanded on the other. Using the designation \( |n_1 n_2 m> \) for the parabolic eigenstates we have

\[
|100>_p = |\psi_+> = \frac{1}{\sqrt{2}} |210>_s - \frac{1}{\sqrt{2}} |200>_s ; \quad E_2^{(1)} = +3F \\
|010>_p = |\psi_-> = \frac{1}{\sqrt{2}} |210>_s + \frac{1}{\sqrt{2}} |200>_s ; \quad E_2^{(1)} = -3F \\
|001>_p = |211>_s ; \quad E_2^{(1)} = 0 \\
|00–1>_p = |21–1>_s ; \quad E_2^{(1)} = 0
\]
We have emphasized that the orbital eigenfunctions are symmetric about the origin and therefore do not have permanent electric dipole moments, while the parabolic eigenfunctions can be highly asymmetric. Mathematically, we can see that any linear combination of orbital eigenfunctions, all of which correspond to the same eigenenergy, will also be an eigenfunction corresponding to the same eigenenergy. It is therefore not surprising that the charge distribution of the parabolic states are, in general, asymmetric. Below we show the electron probability density for the parabolic state, $|100\rangle_p$. Note that the electron is most often, in fact, almost always, found above the xy-plane so that virtually the entire charge density is above the xy-plane.

$n_1 = 1 ; n_2 = 0 ; m = 0 ; n = 2$