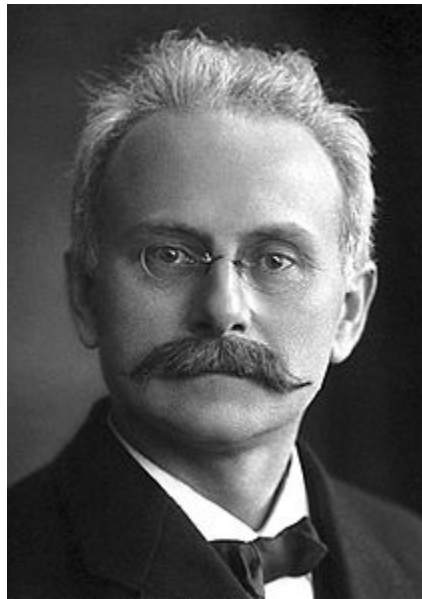


Stark effect in hydrogen
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Although the splitting up of spectral lines in a magnetic field was discovered by Zeeman as early as 1897, some 16 years elapsed before anyone succeeded in showing that a similar effect is produced when a source of light is placed in an electric field. In 1913, Stark demonstrated that every line of the Balmer series of hydrogen, when excited in a strong electric field of at least 10^5 V/cm, is split into a number of components.

Johannes Stark (15 April 1874 – 21 June 1957) was a German physicist, and Physics Nobel Prize laureate who was closely involved with the *Deutsche Physik* movement under the Nazi regime.

http://en.wikipedia.org/wiki/Johannes_Stark



1 Hamiltonian for the hydrogen atom in the presence of an electric field

\hat{H}_0 is the Hamiltonian of the hydrogen atom. We apply an external electric field $\boldsymbol{\varepsilon}$ (along the z axis) to the hydrogen atom, producing the Stark effect.

$$\hat{H} = \hat{H}_0 + \hat{H}_1.$$

$$\hat{H}_1 = -\hat{\boldsymbol{\mu}}_e \cdot \boldsymbol{\varepsilon} = -(-e\hat{\boldsymbol{r}}) \cdot \boldsymbol{\varepsilon} = e\boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{z}}.$$

where $-e$ ($e > 0$) is the electron charge and $\mu_e (= -e\mathbf{r})$ is an electric dipole moment. The vector \mathbf{r} is the position vector of electron. The proton (charge e) is located at the origin. The eigenstate of \hat{H}_0 is given by $|n, l, m\rangle$ with the energy

$$E_n^{(0)} = -\frac{R}{n^2}.$$

where R is the Rydberg constant. $R = 13.60569193$ eV.

In the presence of \hat{H}_1 , the full spherical symmetry of the Hamiltonian is destroyed by the external electric field that selects the positive z -direction, but \hat{H} is still invariant under the rotation around the z axis.

$$|\psi'\rangle = \hat{R}_z |\psi\rangle,$$

$$\langle \psi' | \hat{H} | \psi' \rangle = \langle \psi | \hat{H} | \psi \rangle,$$

or

$$\langle \psi | \hat{R}_z^\dagger \hat{H} \hat{R}_z | \psi \rangle = \langle \psi | \hat{H} | \psi \rangle,$$

or

$$\hat{R}_z^\dagger \hat{H} \hat{R}_z = \hat{H},$$

or

$$[\hat{H}, \hat{R}_z] = 0.$$

Since

$$\hat{R}_z = \exp\left[-\frac{i}{\hbar} \hat{L}_z \delta\theta\right] \approx \hat{1} - \frac{i}{\hbar} \hat{L}_z \delta\theta.$$

We have

$$[\hat{H}, \hat{L}_z] = 0, \quad \text{or} \quad [\hat{H}_0 + \hat{H}_1, \hat{L}_z] = 0$$

Since

$$[\hat{H}_0, \hat{L}_x] = 0, \quad [\hat{H}_0, \hat{L}_y] = 0, \quad [\hat{H}_0, \hat{L}_z] = 0$$

then we have

$$[\hat{H}_1, \hat{L}_z] = 0.$$

Since

$$\hat{H}_1 = e\epsilon\hat{z}$$

we also have

$$[\hat{L}_z, \hat{z}] = 0.$$

where

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

2 Selection rules

The selection rules are summarized as follows.

(i) Selection rule-1

$$\langle n, l, m | \hat{z} | n', l', m' \rangle \neq 0,$$

only for $m' = m$.

(ii) Selection rule-2

$$\langle n, l, m | \hat{x} \pm i\hat{y} | n', l', m' \rangle = 0.$$

only for $m' = m \pm 1$.

(iii) Selection rule-3

$$\langle n, l, m | \hat{z} | n', l', m' \rangle = 0$$

unless $l' = l \pm 1$.

3. Derivation of the selection rules from commutation relations

(a) Selection rule 1

We note that the commutation relation $[\hat{L}_z, \hat{z}] = 0$, can be derived from the original definition of the angular momentum.

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

with

$$[\hat{L}_z, \hat{z}] = 0.$$

Using the commutation relation, we calculate the matrix element;

$$\begin{aligned} \langle n, l, m | [\hat{L}_z, \hat{z}] | n', l', m' \rangle &= \langle n, l, m | \hat{L}_z \hat{z} - \hat{z} \hat{L}_z | n', l', m' \rangle \\ &= (m - m') \hbar \langle n, l, m | \hat{z} | n', l', m' \rangle = 0 \end{aligned}$$

Thus,

only for $m' = m$.

$$\langle n, l, m | \hat{z} | n', l', m' \rangle \neq 0$$

(b) Selection rule 2

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

with

$$[\hat{L}_z, \hat{x}] = i\hbar\hat{y}, \quad [\hat{L}_z, \hat{y}] = -i\hbar\hat{x}.$$

From this commutation relation, we have

$$\begin{aligned} \langle n, l, m | [\hat{L}_z, \hat{x}] | n', l', m' \rangle &= \langle n, l, m | \hat{L}_z \hat{x} - \hat{x} \hat{L}_z | n', l', m' \rangle \\ &= (m - m') \hbar \langle n, l, m | \hat{x} | n', l', m' \rangle \\ &= i\hbar \langle n, l, m | \hat{y} | n', l', m' \rangle \end{aligned} \quad (1)$$

and

$$\begin{aligned} \langle n, l, m | [\hat{L}_z, \hat{y}] | n', l', m' \rangle &= \langle n, l, m | \hat{L}_z \hat{y} - \hat{y} \hat{L}_z | n', l', m' \rangle \\ &= (m - m') \hbar \langle n, l, m | \hat{y} | n', l', m' \rangle \\ &= -i\hbar \langle n, l, m | \hat{x} | n', l', m' \rangle \end{aligned} \quad (2)$$

From Eqs.(1) and (2), we get

$$(m - m')^2 \langle n, l, m | \hat{x} | n', l', m' \rangle = i(m - m') \langle n, l, m | \hat{y} | n', l', m' \rangle \\ = \langle n, l, m | \hat{x} | n', l', m' \rangle$$

or

$$[(m - m')^2 - 1] \langle n, l, m | \hat{x} | n', l', m' \rangle = 0$$

For $m' = m \pm 1$, we have

$$\langle n, l, m | \hat{x} \pm i\hat{y} | n', l', m' \rangle = 0.$$

For $m' \neq m \pm 1$

$$\langle n, l, m | \hat{x} | n', l', m' \rangle = \langle n, l, m | \hat{y} | n', l', m' \rangle = 0$$

(c) Selection rule 3

We can show the commutation relation

$$[\hat{L}^2, [\hat{L}^2, \hat{r}]] = 2\hbar^2 (\hat{L}^2 \hat{r} + \hat{r} \hat{L}^2)$$

by using the two methods (i) the commutation relations and (ii) Mathematica.

Using this relation we can calculate the matrix element of the commutation relation

$$\langle n, l, m | [\hat{L}^2, [\hat{L}^2, \hat{r}]] | n', l', m' \rangle = 2\hbar^2 \langle n, l, m | (\hat{L}^2 \hat{r} + \hat{r} \hat{L}^2) | n', l', m' \rangle \\ = 2\hbar^4 [l(l+1) + l'(l'+1)] \langle n, l, m | \hat{r} | n', l', m' \rangle.$$

Noting that

$$2\hbar^2 \langle n, l, m | (\hat{L}^2 \hat{r} + \hat{r} \hat{L}^2) | n', l', m' \rangle = 2\hbar^4 [l(l+1) + l'(l'+1)] \langle n, l, m | \hat{r} | n', l', m' \rangle$$

and

$$\langle n, l, m | [\hat{L}^2, [\hat{L}^2, \hat{r}]] | n', l', m' \rangle = \hbar^2 [l(l+1) - l'(l'+1)] \langle n, l, m | [\hat{L}^2, \hat{r}] | n', l', m' \rangle \\ = \hbar^4 [l(l+1) - l'(l'+1)]^2 [l(l+1)] \langle n, l, m | \hat{r} | n', l', m' \rangle$$

Then we get

$$\{[l(l+1) - l'(l'+1)]^2 - 2l(l+1) - 2l'(l'+1)\} \langle n, l, m | \hat{r} | n', l', m' \rangle = 0.$$

or

$$(l-l'-1)(l-l'+1)(l+l')(l+l'+2)\langle n, l, m | \hat{r} | n', l', m' \rangle = 0$$

This leads to the selection rule

$$\langle n, l, m | \hat{r} | n', l', m' \rangle \neq 0$$

only for $l' = l \pm 1$.

((Proof))

(i) Commutation relations

$$[\hat{L}^2, [\hat{L}^2, \hat{z}] = 2\hbar^2(\hat{z}\hat{L}^2 + \hat{L}^2\hat{z})$$

((Proof)) Griffiths, Introduction to Quantum Mechanics

We prove this by using a various kind of commutation relations.

$$\begin{aligned} [\hat{L}^2, \hat{z}] &= [\hat{L}_x^2, \hat{z}] + [\hat{L}_y^2, \hat{z}] + [\hat{L}_z^2, \hat{z}] \\ &= \hat{L}_x[\hat{L}_x, \hat{z}] + [\hat{L}_x, \hat{z}]\hat{L}_x + \hat{L}_y[\hat{L}_y, \hat{z}] + [\hat{L}_y, \hat{z}]\hat{L}_y + \hat{L}_z[\hat{L}_z, \hat{z}] + [\hat{L}_z, \hat{z}]\hat{L}_z \\ &= i\hbar(-\hat{L}_x\hat{y} - \hat{y}\hat{L}_x + \hat{L}_y\hat{x} + \hat{x}\hat{L}_y) \end{aligned}$$

We note that

$$\hat{L}_x\hat{y} = [\hat{L}_x, \hat{y}] + \hat{y}\hat{L}_x = i\hbar\hat{z} + \hat{y}\hat{L}_x$$

$$\hat{L}_y\hat{x} = [\hat{L}_y, \hat{x}] + \hat{x}\hat{L}_y = -i\hbar\hat{z} + \hat{x}\hat{L}_y$$

Then we get

$$\begin{aligned} [\hat{L}^2, \hat{z}] &= i\hbar[-(i\hbar\hat{z} + \hat{y}\hat{L}_x) - \hat{y}\hat{L}_x + (-i\hbar\hat{z} + \hat{x}\hat{L}_y) + \hat{x}\hat{L}_y] \\ &= 2i\hbar(\hat{x}\hat{L}_y - \hat{y}\hat{L}_x - i\hbar\hat{z}) \end{aligned}$$

Similarly,

$$[\hat{L}^2, \hat{x}] = 2i\hbar(\hat{y}\hat{L}_z - \hat{z}\hat{L}_y - i\hbar\hat{x})$$

and

$$[\hat{L}^2, y] = 2i\hbar(z\hat{L}_x - x\hat{L}_z - i\hbar\hat{y})$$

where

$$[\hat{L}_x, \hat{z}] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}] = [\hat{y}\hat{p}_z, \hat{z}] - [\hat{z}\hat{p}_y, \hat{z}] = \hat{y}[\hat{p}_z, \hat{z}] = -i\hbar\hat{y}.$$

$$[\hat{L}_y, \hat{z}] = [\hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \hat{z}] = -[x\hat{p}_z, \hat{z}] = -\hat{x}[\hat{p}_z, \hat{z}] = -\frac{\hbar}{i}\hat{x} = i\hbar\hat{x}.$$

$$[\hat{L}_z, \hat{z}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{z}] = -[\hat{y}\hat{p}_x, \hat{z}] = 0.$$

$$[\hat{L}_x, \hat{x}] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{x}] = 0.$$

$$[\hat{L}_y, \hat{x}] = [\hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \hat{x}] = [\hat{z}\hat{p}_x, \hat{x}] = \frac{\hbar}{i}\hat{z} = -i\hbar\hat{z}.$$

$$[\hat{L}_z, \hat{x}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{x}] = -[\hat{y}\hat{p}_x, \hat{x}] = i\hbar\hat{y}.$$

$$[\hat{L}_x, \hat{y}] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{y}] = i\hbar\hat{z}.$$

$$[\hat{L}_y, \hat{y}] = [\hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \hat{y}] = 0.$$

$$[\hat{L}_z, \hat{y}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}] = -i\hbar\hat{x}.$$

Then we get

$$\begin{aligned}
[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{z}] &= 2i\hbar\{[\hat{\mathbf{L}}^2, \hat{x}\hat{L}_y] - [\hat{\mathbf{L}}^2, \hat{y}\hat{L}_x] - i\hbar[\hat{\mathbf{L}}^2, \hat{z}]\} \\
&= 2i\hbar\{[\hat{\mathbf{L}}^2, \hat{x}]\hat{L}_y + \hat{x}[\hat{\mathbf{L}}^2, \hat{L}_y] - [\hat{\mathbf{L}}^2, \hat{y}]\hat{L}_x - \hat{y}[\hat{\mathbf{L}}^2, \hat{L}_x] - i\hbar[\hat{\mathbf{L}}^2, \hat{z}]\} \\
&= 2i\hbar\{2i\hbar(\hat{y}\hat{L}_z - \hat{z}\hat{L}_y - i\hbar\hat{x})\hat{L}_y - 2i\hbar(\hat{z}\hat{L}_x - \hat{x}\hat{L}_z - i\hbar\hat{y})\hat{L}_x \\
&\quad - i\hbar(\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2)\} \\
&= -2\hbar^2\{2(\hat{y}\hat{L}_z\hat{L}_y - \hat{z}\hat{L}_y^2 - i\hbar\hat{x}\hat{L}_y) - 2(\hat{z}\hat{L}_x^2 - \hat{x}\hat{L}_z\hat{L}_x - i\hbar\hat{y}\hat{L}_x) \\
&\quad - (\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2)\} \\
&= -2\hbar^2\{2(\hat{y}\hat{L}_z - i\hbar\hat{x})\hat{L}_y - 2\hat{z}(\hat{L}_x^2 + \hat{L}_y^2) + 2(\hat{x}\hat{L}_z + i\hbar\hat{y})\hat{L}_x \\
&\quad - (\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2)\} \\
&= -2\hbar^2\{2\hat{L}_z\hat{y}\hat{L}_y - 2\hat{z}(\hat{\mathbf{L}}^2 - \hat{L}_z^2) + 2\hat{L}_z\hat{x}\hat{L}_x \\
&\quad - (\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2)\} \\
&= -2\hbar^2\{2\hat{L}_z(\hat{x}\hat{L}_x + \hat{y}\hat{L}_y + \hat{z}\hat{L}_z) - 2\hat{L}_z\hat{z}\hat{L}_z - 2\hat{z}(\hat{\mathbf{L}}^2 - \hat{L}_z^2) - (\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2)\}
\end{aligned}$$

or

$$\begin{aligned}
[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{z}] &= -2\hbar^2\{-2\hat{L}_z\hat{z}\hat{L}_z - 2\hat{z}\hat{\mathbf{L}}^2 + 2\hat{z}\hat{L}_z^2 - (\hat{\mathbf{L}}^2\hat{z} - \hat{z}\hat{\mathbf{L}}^2)\} \\
&= 2\hbar^2(\hat{z}\hat{\mathbf{L}}^2 + \hat{\mathbf{L}}^2\hat{z})
\end{aligned}$$

where we use the relations,

$$\hat{x}\hat{L}_x + \hat{y}\hat{L}_y + \hat{z}\hat{L}_z = 0$$

$$[\hat{\mathbf{L}}^2, \hat{L}_x] = [\hat{\mathbf{L}}^2, \hat{L}_y] = [\hat{\mathbf{L}}^2, \hat{L}_z] = 0$$

$$[\hat{L}_z, \hat{z}] = 0$$

and

$$[\hat{\mathbf{L}}^2, \hat{z}] = 2i\hbar(\hat{x}\hat{L}_y - \hat{y}\hat{L}_x - i\hbar\hat{z})$$

$$[\hat{\mathbf{L}}^2, \hat{x}] = 2i\hbar(\hat{y}\hat{L}_z - \hat{z}\hat{L}_y - i\hbar\hat{x})$$

$$[\hat{\mathbf{L}}^2, \hat{y}] = 2i\hbar(\hat{z}\hat{L}_x - \hat{x}\hat{L}_z - i\hbar\hat{y})$$

(ii) **Mathematica**

Using the Mathematica, we show that the above commutations are valid.

$$[\hat{L}_z, \hat{z}] = 0.$$

$$[\hat{L}_z, \hat{x}] = i\hbar \hat{y}, \quad [\hat{L}_z, \hat{y}] = -i\hbar \hat{x}.$$

$$[\hat{L}^2, [\hat{L}^2, \hat{r}]] = 2\hbar^2 (\hat{L}^2 \hat{r} + \hat{r} \hat{L}^2)$$

((Mathematica))

```
Clear["Global`"];

<< VectorAnalysis`;

SetCoordinates[Cartesian[x, y, z]];

ux = {1, 0, 0}; uy = {0, 1, 0}; uz = {0, 0, 1}; r = {x, y, z};

Lx := (ux.(-i h Cross[r, Grad[#]]) &) // Simplify;
Ly := (uy.(-i h Cross[r, Grad[#]]) &) // Simplify;
Lz := (uz.(-i h Cross[r, Grad[#]]) &) // Simplify;

Lsq := (Nest[Lx, #, 2] + Nest[Ly, #, 2] + Nest[Lz, #, 2]) &;

eq1 = (Lz[z x[x, y, z]] - z Lz[x[x, y, z]]) // FullSimplify
0

eq2 = Lz[x x[x, y, z]] - x Lz[x[x, y, z]] - i h y x[x, y, z] // Simplify
0

eq3 = Lz[y x[x, y, z]] - y Lz[x[x, y, z]] + i h x x[x, y, z] // Simplify
0

eq4 = 2 h^2 (Lsq[x x[x, y, z]] + x Lsq[x[x, y, z]]) // Simplify;

eq5 = Lsq[Lsq[x x[x, y, z]]] - Lsq[x Lsq[x[x, y, z]]] - Lsq[x Lsq[x[x, y, z]]] +
x Lsq[Lsq[x[x, y, z]]] // Simplify;

eq4 - eq5
0
```

4. Selection rule derived from the parity operator

$\hat{\pi}$ is the parity operator:

$$\hat{\pi}^+ = \hat{\pi} = \hat{\pi}^{-1},$$

\hat{z} is the parity odd operator with

$$\hat{\pi} \hat{z} \hat{\pi} = -\hat{z},$$

and

$$\hat{\pi}|n, l, m\rangle = (-1)^l |n, l, m\rangle,$$

or

$$\langle n, l, m | \hat{\pi} = (-1)^l \langle n, l, m |.$$

Then we have

$$\langle n, l, m | \hat{z} | n', l', m' \rangle = 0 \text{ for the } l\text{-state and } l'\text{-state with the same parity.}$$

The reason is as follows.

$$\langle n, l, m | \hat{\pi} \hat{z} \hat{\pi} | n', l', m' \rangle = -\langle n, l, m | \hat{z} | n', l', m' \rangle,$$

or

$$\langle n, l, m | \hat{z} | n', l', m' \rangle = (-1)^{l+l'+1} \langle n, l, m | \hat{z} | n', l', m' \rangle.$$

When $l + l' + 1 = 2k + 1$ (odd numbers), or $l + l' = 2k$ (even number), we have

$$\langle n, l, m | \hat{z} | n', l', m' \rangle = 0.$$

5. Selection rule for the Wigner-Eckart theorem

$$\langle l', m' | \hat{T}_q^{(k)} | \alpha; l, m \rangle \neq 0$$

only if

$$m' - m - q = 0$$

(selection rule)

$$l' = l + k, l + k - 1, \dots, |l - k|$$

where

$$\hat{T}_0^{(1)} = \hat{z}.$$

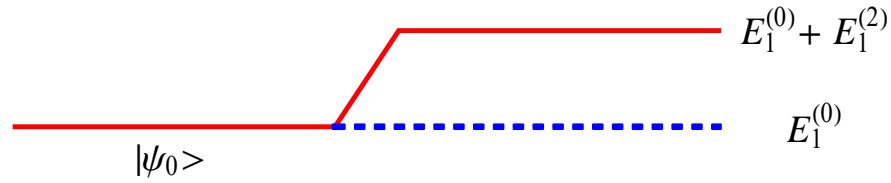
$$\hat{T}_1^{(1)} = -\frac{\hat{x} + i\hat{y}}{\sqrt{2}}$$

$$T_{-1}^{(1)} = \frac{\hat{x} - i\hat{y}}{\sqrt{2}}$$

6. The Stark effect on the $n = 1$ level

The ground state is non-degenerate.

$$|\psi_0\rangle = |n=1, l=0, m=0\rangle$$



The energy to the first order:

$$E_1^{(0)} = -R$$

$$E_1^{(1)} = \langle \psi_0 | \hat{H}_1 | \psi_0 \rangle = \langle 1,0,0 | \hat{H}_1 | 1,0,0 \rangle = 0$$

$$E_1^{(2)} = e^2 \varepsilon^2 \sum_{n \neq 1, l, m} \frac{|\langle 1,0,0 | \hat{z} | n, l, m \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

where

$$E_n^{(0)} = -\frac{R}{n^2}$$

with

$$a_0 = \frac{\hbar^2}{me^2}, \quad R = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0}.$$

Then we have

$$\Delta E_1 = E_1^{(2)} = -\frac{1}{2} \alpha \varepsilon^2 = e^2 \varepsilon^2 \sum_{n \neq 1, l, m} \frac{|\langle 1,0,0 | \hat{z} | n, l, m \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

or

$$\alpha = -2e^2 \sum_{n \neq 1, l, m} \frac{|\langle 1, 0, 0 | \hat{z} | n, l, m \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

The preceding sum is certainly not zero, since there exist states $|n, l, m\rangle$ whose parity is opposite to that of $|1, 0, 0\rangle$. To the lowest order in ε , the Stark shift of the 1s ground state is quadratic.

((Polarizability))

Electric polarizability is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field, which is applied typically by inserting the molecule in a charged parallel-plate capacitor, but may also be caused by the presence of a nearby ion or dipole. The electronic polarizability α is defined as the ratio of the induced dipole moment P of an atom to the electric field ε that produces this dipole moment.

$$p = \alpha\varepsilon$$

The work done on the system as ε slightly changes to $\varepsilon + d\varepsilon$,

$$dW = -pd\varepsilon = -\alpha\varepsilon d\varepsilon$$

or

$$W = \Delta E = -\frac{1}{2}\alpha\varepsilon^2$$

The energy ΔE is quadratic with respect to the electric field.

6 Polarizability of the 1s-state

$$|\psi_{1s}\rangle = |1, 0, 0\rangle + e\varepsilon \sum_{\substack{n \neq 1 \\ l, m}} |n, l, m\rangle \frac{\langle n, l, m | \hat{z} | 1, 0, 0 \rangle}{E_1^{(0)} - E_n^{(0)}} + \dots$$

The electric field ε causes an induced dipole moment p .

$$p = \langle \psi_{1s} | (-e\hat{z}) | \psi_{1s} \rangle = -2e^2\varepsilon \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2}{E_1^{(0)} - E_n^{(0)}} = \alpha\varepsilon$$

or

$$\alpha = -2e^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

Under the perturbation, the energy shift is given by

$$\Delta E = e^2 \varepsilon^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{\langle n, l, m | \hat{z} | 1, 0, 0 \rangle^2}{E_1^{(0)} - E_n^{(0)}} = -\frac{\alpha \varepsilon^2}{2}$$

((Note-1))

$$\begin{aligned} \langle \psi_{1s} | (-e\hat{z}) | \psi_{1s} \rangle &= (\langle 1, 0, 0 | + e\varepsilon \sum_{\substack{n \neq 1 \\ l, m}} \langle n, l, m | \frac{\langle n, l, m | \hat{z} | 1, 0, 0 \rangle^*}{(E_1^{(0)} - E_n^{(0)})} + \dots) (-e\hat{z}) \\ &\quad \times (\langle 1, 0, 0 \rangle + e\varepsilon \sum_{\substack{n \neq 1 \\ l, m}} |n, l, m\rangle \frac{\langle n, l, m | \hat{z} | 1, 0, 0 \rangle}{(E_1^{(0)} - E_n^{(0)})} + \dots) \end{aligned}$$

((Note-2))

Since

$$\langle 1, 0, 0 | \hat{z} | 1, 0, 0 \rangle = 0 \text{ and } E_n^{(0)} - E_1^{(0)} \geq E_2^{(0)} - E_1^{(0)} > 0$$

we have

$$\begin{aligned} \alpha &= 2e^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2}{E_n^{(0)} - E_1^{(0)}} \leq \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \sum_{\substack{n \neq 1 \\ l, m}} |\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2 \\ &= \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \sum_{\substack{n, \\ l, m}} |\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2 \end{aligned}$$

Here

$$\sum_{\substack{n, \\ l, m}} |\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2 = \sum_{\substack{n, \\ l, m}} \langle 1, 0, 0 | \hat{z} | n, l, m \rangle \langle n, l, m | \hat{z} | 1, 0, 0 \rangle = \langle 1, 0, 0 | \hat{z}^2 | 1, 0, 0 \rangle$$

Then we have

$$\alpha \leq \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \sum_{\substack{n, \\ l, m}} |\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2 = \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \langle 1, 0, 0 | \hat{z}^2 | 1, 0, 0 \rangle$$

$$\alpha \leq \frac{2e^2}{\frac{e^2}{2a_0} \left(1 - \frac{1}{4}\right)} a_0^2 = \frac{16}{3} a_0^3 = 5.33 a_0^3$$

which is consistent with the experimentally observed value: $\alpha = 4.5 a_0^3$. Note that a_0 is the Bohr radius, $a_0 = a_B = 0.52917721067 \text{ \AA}$.

$$\langle 1, 0, 0 | \hat{z}^2 | 1, 0, 0 \rangle = a_0^2$$

((Note)) Evaluation of $\langle r^2 \rangle$

Another method to calculate the value α is shown as follows. Here we use the formula

$$\langle r^2 \rangle = \frac{a^2}{2Z^2} n^2 [5n^2 + 1 - 3l(l+1)].$$

For $n = 1$, $Z = 1$, and $l = 0$, the radius R can be evaluated as

$$R = \sqrt{\langle r^2 \rangle} = \sqrt{3} a_0$$

for $a = a_B$. Then α is calculated as

$$\alpha = R^3 = 3\sqrt{3} a_0^3 = 5.196 a_0^3$$

Experimentally, α for hydrogen is $\alpha = 6.67 \times 10^{-25} \text{ cm}^3 = 4.50 a_0^3$.

((Bethe-Salpeter))

Hans Albrecht Bethe (July 2, 1906 – March 6, 2005) was a German-American physicist, and Nobel laureate in physics for his work on the theory of stellar nucleosynthesis. A versatile theoretical physicist, Bethe also made important contributions to quantum electrodynamics, nuclear physics, solid-state physics and particle astrophysics. For most of his career, Bethe was a professor at Cornell University.



http://en.wikipedia.org/wiki/Hans_Bethe

How can we calculate the exact value of α ?

$$\alpha = 2e^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2}{E_n^{(0)} - E_1^{(0)}} = 2e^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle n, l, m | \hat{z} | 1, 0, 0 \rangle|^2}{E_n^{(0)} - E_1^{(0)}}$$

$$\langle n, l, m | \hat{z} | 1, 0, 0 \rangle = \int d^3 r R_{nl}^*(r) Y_l^m(\theta, \phi) r \cos \theta [R_{10}(r) Y_0^0(\theta, \phi)]$$

Here

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, \quad \cos \theta = \sqrt{\frac{4\pi}{3}} Y_1^0(\theta, \phi)$$

$$\langle n, l, m | \hat{z} | 1, 0, 0 \rangle = \int d\Omega Y_l^m(\theta, \phi) \frac{1}{\sqrt{3}} Y_1^0(\theta, \phi) \int_0^\infty r^3 dr R_{nl}(r) R_{10}(r)$$

$$\int d\Omega Y_l^m(\theta, \phi) \frac{1}{\sqrt{3}} Y_1^0(\theta, \phi) = \frac{1}{\sqrt{3}} \delta_{l,1} \delta_{m,0}$$

Then we have

$$\langle n, l, m | \hat{z} | 1, 0, 0 \rangle = \frac{1}{\sqrt{3}} \delta_{l,1} \delta_{m,0} \int_0^\infty r^3 dr R_{n1}(r) R_{10}(r)$$

or

$$|\langle n, 1, 0 | \hat{z} | 1, 0, 0 \rangle|^2 = \frac{1}{3} \left[\int_0^\infty r^3 dr R_{n1}(r) R_{10}(r) \right]^2 = a_0^2 f(n)$$

where $f(n)$ is obtained by H.A. Bethe and E.E. Salpeter [Quantum Mechanics of One- and Two Electron Atoms, Academic Press, New York, 1957, p.262]

$$f(n) = \frac{1}{3} \frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}}$$

$$E_n = -\frac{m_0 e^4}{2n^2 \hbar^2} = -\frac{e^2}{2n^2 a_0}$$

$$E_n^{(0)} - E_1^{(0)} = \frac{e^2}{2a_0} \left(1 - \frac{1}{n^2}\right)$$

Then we have

$$\alpha = 2e^2 \sum_{n \neq 1} \frac{|\langle n, 1, 0 | \hat{z} | 1, 0, 0 \rangle|^2}{E_n^{(0)} - E_1^{(0)}} = 4a_0^3 \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1} = 4a_0^3 0.915806 = 3.66326a_0^3$$

((Mathematica))

Stark effect with $n = 1$

```
Clear["Global`*"];
R[n_, l_, r_] :=  $\frac{1}{\sqrt{(n+l)!}} \left( 2^{1+l} a_0^{-l-\frac{3}{2}} e^{-\frac{r}{a_0 n}} n^{-l-2} r^l \sqrt{(n-l-1)!} \text{LaguerreL}[-1+n-l, 1+2l, \frac{2r}{a_0 n}] \right);$ 
Y[l_, m_, \theta_, \phi_] := SphericalHarmonicY[l, m, \theta, \phi];
\psi[n_, l_, m_, r_, \theta_, \phi_] := R[n, l, r] Y[l, m, \theta, \phi]
f[n1_, l1_, m1_, n2_, l2_, m2_, r_, \theta_, \phi_] =
(-1)^{m1} \psi[n1, l1, -m1, r, \theta, \phi] r Cos[\theta] \psi[n2, l2, m2, r, \theta, \phi] r^2 Sin[\theta] // Simplify;
```

Integral calculation

```
g[n1_, l1_, m1_, n2_, l2_, m2_] :=
Simplify[Integrate[Integrate[Integrate[ $\frac{f[n1, l1, m1, n2, l2, m2, r, \theta, \phi]}{a_0}$ , {\phi, 0, 2\pi}], {\theta, 0, \pi}], {r, 0, \infty}], a_0 > 0];
```

Beth's formula

$$h[n_] = \frac{1}{3} \frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}};$$

```
Table[{n, 1, g[n, 1, 0, 1, 0, 0]^2 // N, h[n] // N}, {n, 2, 10}] // TableForm
```

2	1	0.554929	0.554929
3	1	0.0889893	0.0889893
4	1	0.0309238	0.0309238
5	1	0.0145191	0.0145191
6	1	0.00802234	0.00802234
7	1	0.00491424	0.00491424
8	1	0.00323396	0.00323396
9	1	0.00224381	0.00224381
10	1	0.00162158	0.00162158

$$4 \sum_{n=2}^{\infty} \frac{n^2 h[n]}{n^2 - 1} // N$$

3.66326

7 Stark effect on the $n = 2$ level

We now consider the state with $n = 2$.

$n = 2$ state (4 states-degeneracy):

$l = 1$ ($m = \pm 1, 0$): p -state (3 states)

$l = 0$ ($m = 0$): s -state (1 state)

Note that

$$E_2^{(0)} = -\frac{R}{2^2}$$

is the eigenvalue of \hat{H}_0 . The degenerate system with the four states:

$$|n, l, m\rangle = |2, 0, 0\rangle, |2, 1, 1\rangle, |2, 1, 0\rangle, |2, 1, -1\rangle$$

with the same energy. For convenience we introduce the basis as

$$|\psi_1^{(0)}\rangle = |2,0,0\rangle \quad \text{even state}$$

$$|\psi_2^{(0)}\rangle = |2,1,1\rangle$$

$$|\psi_3^{(0)}\rangle = |2,1,0\rangle \quad \text{odd states}$$

$$|\psi_4^{(0)}\rangle = |2,1,-1\rangle$$

From the selection rule, we have

$$\langle 2,1,m|\hat{z}|2,0,m'\rangle = \langle 2,1,m|\hat{z}|2,0,m\rangle\delta_{m,m'},$$

$$\langle 2,1,m|\hat{z}|2,1,m'\rangle = 0,$$

$$\langle 2,0,0|\hat{z}|n,0,0\rangle = 0.$$

The matrix of \hat{H}_1 based on these bases is given by

$$\begin{pmatrix} 0 & 0 & (\hat{H}_1)_{13} & 0 \\ 0 & 0 & 0 & 0 \\ (\hat{H}_1)_{31} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

where

$$(\hat{H}_1)_{31} = e\varepsilon\langle\psi_3^{(0)}|\hat{z}|\psi_1^{(0)}\rangle = -3e\varepsilon a_0 = -E_0,$$

or

$$E_0 = 3e\varepsilon a_0 (>0).$$

Note that

$$\begin{aligned} \langle\psi_3^{(0)}|\hat{z}|\psi_1^{(0)}\rangle &= \langle 2,1,0|\hat{z}|2,0,0\rangle = \int d\mathbf{r}\langle 2,1,0|\mathbf{r}\rangle\langle\mathbf{r}|\hat{z}|2,0,0\rangle \\ &= \iiint r \cos\theta R_{21}(r)^* [Y_1^0(\theta,\phi)]^* R_{20}(r) Y_0^0(\theta,\phi) r^2 \sin\theta dr d\theta d\phi \\ &= -3a_0 \end{aligned}$$

Matrix elements of $\langle n,l',m'|\hat{H}_1|n,l,m\rangle$ is given by

$$\begin{array}{cccc}
& |2,1,1\rangle & |2,1,0\rangle & |2,1,-1\rangle & |2,0,0\rangle \\
\langle 2,1,1| & 0 & 0 & 0 & 0 \\
\langle 2,1,0| & 0 & 0 & 0 & -E_0 \\
\langle 2,1,-1| & 0 & 0 & 0 & 0 \\
\langle 2,0,0| & 0 & -E_0 & 0 & 0
\end{array}$$

where

$$\langle 2,1,0|\hat{H}|2,0,0\rangle = -3e\epsilon a_0 = -E_0.$$

The reduced matrix:

$$\begin{array}{cc}
& |2,1,0\rangle & |2,0,0\rangle \\
\langle 2,1,0| & 0 & -E_0 \\
\langle 2,0,0| & -E_0 & 0
\end{array}$$

We find that

$$\hat{H}_1|\psi_1^{(0)}\rangle = -E_0|\psi_3^{(0)}\rangle,$$

$$\hat{H}_1|\psi_2^{(0)}\rangle = 0,$$

$$\hat{H}_1|\psi_3^{(0)}\rangle = -E_0|\psi_1^{(0)}\rangle,$$

$$\hat{H}_1|\psi_4^{(0)}\rangle = 0.$$

$|\psi_2^{(0)}\rangle$ and $|\psi_4^{(0)}\rangle$ are the eigenstates of \hat{H}_1 with the energy 0.

We now consider the matrix of \hat{H}_1 in terms of the basis $|\psi_1^{(0)}\rangle$ and $|\psi_3^{(0)}\rangle$

$$\hat{H}_{1r} = \begin{pmatrix} 0 & -E_0 \\ -E_0 & 0 \end{pmatrix},$$

$$|\varphi_1\rangle = \hat{U}|\psi_1^{(0)}\rangle \text{ and } |\varphi_3\rangle = \hat{U}|\psi_3^{(0)}\rangle,$$

with

$$\hat{U} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}.$$

For $\lambda = -E_0$ (the lowest level)

$$|\varphi_1\rangle = \hat{U}|\psi_1^{(0)}\rangle = \begin{pmatrix} U_{11} \\ U_{12} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}.$$

For $\lambda = E_0$, (the highest level)

$$|\varphi_3\rangle = \hat{U}|\psi_3^{(0)}\rangle = \begin{pmatrix} U_{12} \\ U_{22} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}.$$

The degenerate level of $n = 2$ splits into the three levels:

(i) The round state: $E = E_2^{(0)} - E_0$ (symmetric state)

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}}(|\psi_1^{(0)}\rangle + |\psi_3^{(0)}\rangle).$$

(ii) The first excited state with $E_2^{(0)}$ (double-degeneracy)

$$|\psi_2^{(0)}\rangle \text{ and } |\psi_4^{(0)}\rangle.$$

(iii) The second excited state with $E_2^{(0)} + E_0$ (anti-symmetric state)

$$|\varphi_3\rangle = \frac{1}{\sqrt{2}}(|\psi_1^{(0)}\rangle - |\psi_3^{(0)}\rangle).$$

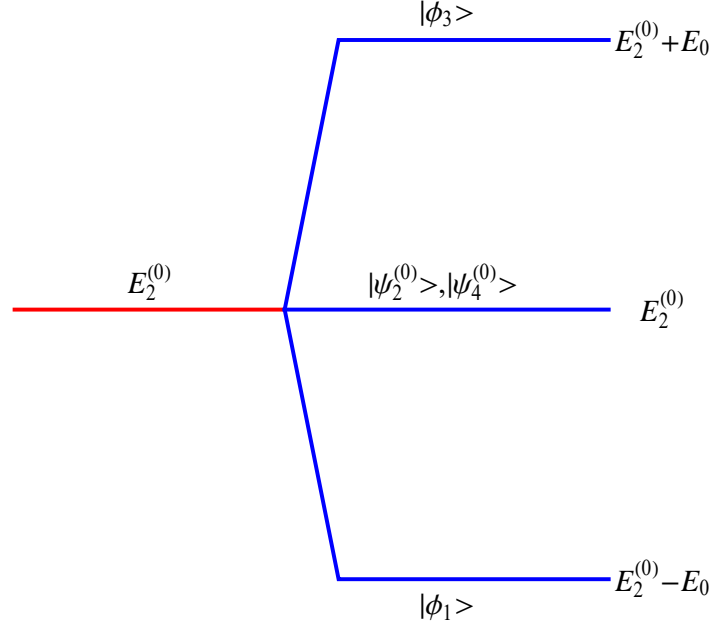


Fig. Energy splitting (Stark effect with $n = 2$). $E_0 = 3e\epsilon\alpha_0$.

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}[|200\rangle + |210\rangle], \quad |\phi_3\rangle = \frac{1}{\sqrt{2}}[|200\rangle - |210\rangle]$$

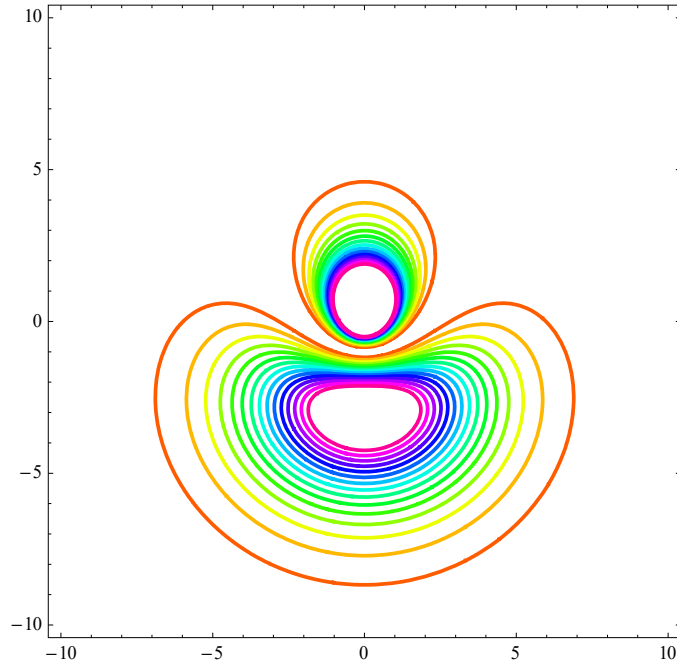
$$|\psi_2^{(0)}\rangle = |211\rangle, \quad |\psi_4^{(0)}\rangle = |21-1\rangle$$

8 Charge density distribution for the Stark effect with $n = 2$

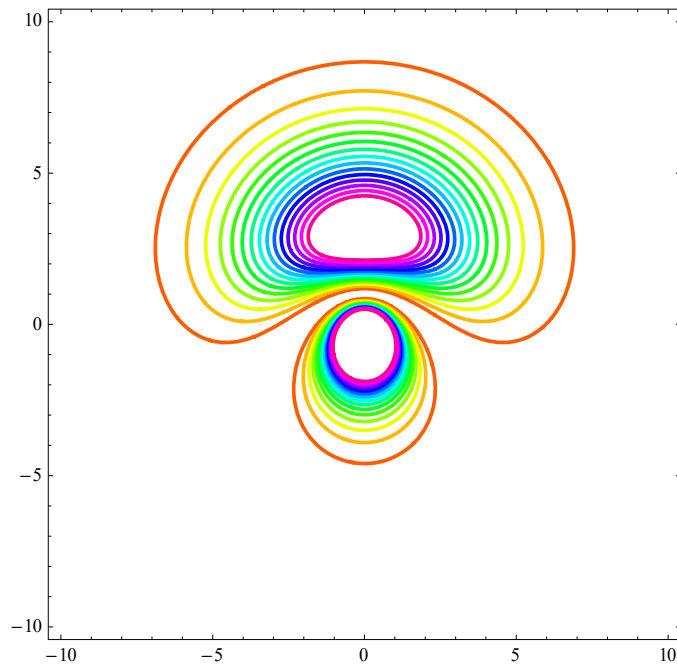
The charge density distribution for the $|\phi_1\rangle$, $|\phi_3\rangle$, $|\psi_2^{(0)}\rangle$ and $|\psi_4^{(0)}\rangle$ is evaluated from the CountourPlot (Mathematica) of

$$\langle \mathbf{r} | \phi_1 \rangle|^2, \quad \langle \mathbf{r} | \phi_3 \rangle|^2, \quad \langle \mathbf{r} | \psi_2^{(0)} \rangle|^2, \quad \text{and} \quad \langle \mathbf{r} | \psi_4^{(0)} \rangle|^2,$$

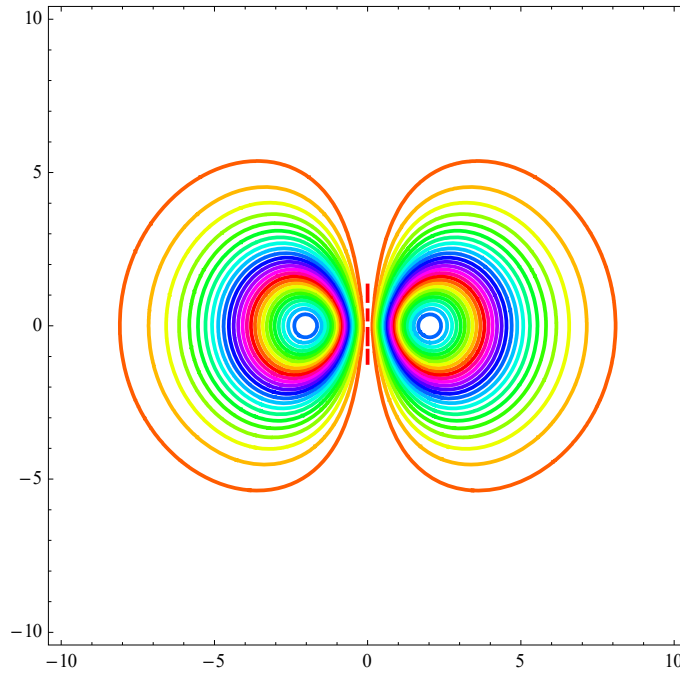
where $y = 0$, in the x - z plane.



ContourPlot of $\langle \mathbf{r} | \varphi_1 \rangle^2$ with $y = 0$, in the x - z plane. When the electric field is applied along the z axis, the average position of electrons shifts to the $(-z)$ direction. The energy eigenvalue is $E = E_2^{(0)} - E_0$.



ContourPlot of $\langle \mathbf{r} | \varphi_3 \rangle^2$ with $y = 0$, in the x - z plane. When the electric field is applied along the z axis, the average position of electrons shifts to the z direction. The energy eigenvalue is $E = E_2^{(0)} + E_0$.



ContourPlot of $|\langle \mathbf{r} | \psi_2^{(0)} \rangle|^2 = |\langle \mathbf{r} | \psi_4^{(0)} \rangle|^2$ with $y = 0$, in the $x-z$ plane. When the electric field is applied along the z axis, the average position of electrons remains unshifted in the direction to the z axis. The energy eigenvalue is $E = E_2^{(0)}$.

Two of the four degenerate states for $n = 2$ ($|\psi_2^{(0)}\rangle$ and $|\psi_4^{(0)}\rangle$) are unaffected by the electric field to the first order, and the other two linear combinations

$$|\varphi_1\rangle = \frac{1}{\sqrt{2}} (|\psi_1^{(0)}\rangle + |\psi_3^{(0)}\rangle) \quad (E = E_2^{(0)} - E_0),$$

and

$$|\varphi_3\rangle = \frac{1}{\sqrt{2}} (|\psi_1^{(0)}\rangle - |\psi_3^{(0)}\rangle) \quad (E = E_2^{(0)} + E_0).$$

This means that the hydrogen atom in this unperturbed state behaves as though it has a permanent electric-dipole moment of magnitude $3ea_0$, which can be oriented in three different ways; one state parallel to the external electric field, one state anti-parallel to the field, two states with zero component along the field (Schiff).

((**Mathematica**)) The eigenvalue problem for $n = 2$ is solved using the Mathematica.

Calculation of matrix element for the Stark effect with $n = 1$

```

R[n_, l_, r_] :=
  1
  -----
  Sqrt[(n + l) !]
  ( 21+l a0-l-3/2 e-r/a0 n n-l-2 rl Sqrt[(n - l - 1) !]
    LaguerreL[-1 + n - l, 1 + 2 l,  $\frac{2 r}{a0 n}$ ] )
Y[l_, m_,  $\theta$ _,  $\phi$ _] := SphericalHarmonicY[l, m,  $\theta$ ,  $\phi$ ];
 $\psi$ [n_, l_, m_, r_,  $\theta$ _,  $\phi$ _] := R[n, l, r] Y[l, m,  $\theta$ ,  $\phi$ ];
f[n1_, l1_, m1_, n2_, l2_, m2_, r_,  $\theta$ _,  $\phi$ _] =
  (-1)m1  $\psi$ [n1, l1, -m1, r,  $\theta$ ,  $\phi$ ] r Cos[ $\theta$ ]  $\psi$ [n2, l2, m2, r,  $\theta$ ,  $\phi$ ]
  r2 Sin[ $\theta$ ] // Simplify;

Simplify[
  Integrate[
    Integrate[Integrate[f[2, 1, 0, 2, 0, 0, r,  $\theta$ ,  $\phi$ ],
      { $\phi$ , 0, 2  $\pi$ }], { $\theta$ , 0,  $\pi$ }], {r, 0,  $\infty$ }], a0 > 0]
-3 a0

```


$E_0 = 3 \epsilon a_0 \epsilon$; Eigenvalue problem for the simplified system

$$H_{22} = \{\{0, -E_0\}, \{-E_0, 0\}\}$$

$$\{\{0, -E_0\}, \{-E_0, 0\}\}$$

$$eq1 = \text{Eigensystem}[H_{22}]$$

$$\{\{-E_0, E_0\}, \{\{1, 1\}, \{-1, 1\}\}\}$$

$$\psi_1 = \text{Normalize}[eq1[[2, 1]]]$$

$$\left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}$$

$$\psi_2 = -\text{Normalize}[eq1[[2, 2]]]$$

$$\left\{ \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right\}$$

$$U^T = \{\psi_1, \psi_2\}$$

$$\left\{ \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}, \left\{ \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right\} \right\}$$

$$U = \text{Transpose}[U^T]$$

$$\left\{ \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}, \left\{ \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right\} \right\}$$

$$U^H = U^T$$

$$\left\{ \left\{ \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right\}, \left\{ \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right\} \right\}$$

$$U^H \cdot U$$

$$\{\{1, 0\}, \{0, 1\}\}$$

9 $n = 3$ Stark effect

We consider the case of $n = 3$.

$n = 3$ state (9 states degenerate):

$$\begin{array}{ll} l = 2 (m = \pm 2, \pm 1, 0): & d\text{-state (5 states)} \\ l = 1 (m = \pm 1, 0): & p\text{-state 3 states} \\ l = 0 (m = 0): & s\text{-state (1 state)} \end{array}$$

Note that

$$E_3^{(0)} = -\frac{R}{3^2},$$

is the eigenvalue of \hat{H}_0 .

Matrix elements of H_1 :

	$ 3,2,2\rangle$	$ 3,2,1\rangle$	$ 3,2,0\rangle$	$ 3,2,-1\rangle$	$ 3,2,-2\rangle$	$ 3,1,1\rangle$	$ 3,1,0\rangle$	$ 3,1,-1\rangle$	$ 3,0,0\rangle$
$\langle 3,2,2 $	0	0	0	0	0	0	0	0	0
$\langle 3,2,1 $	0	0	0	0	0	$-\frac{9}{2}e\epsilon\alpha_0$	0	0	0
$\langle 3,2,0 $	0	0	0	0	0	0	$-3\sqrt{3}e\epsilon\alpha_0$	0	0
$\langle 3,2,-1 $	0	0	0	0	0	0	0	$-\frac{9}{2}e\epsilon\alpha_0$	0
$\langle 3,2,-2 $	0	0	0	0	0	0	0	0	0
$\langle 3,1,1 $	0	$-\frac{9}{2}e\epsilon\alpha_0$	0	0	0	0	0	0	0
$\langle 3,1,0 $	0	0	$-3\sqrt{3}e\epsilon\alpha_0$	0	0	0	0	0	$-3\sqrt{6}e\epsilon\alpha_0$
$\langle 3,1,-1 $	0	0	0	$-\frac{9}{2}e\epsilon\alpha_0$	0	0	0	0	0
$\langle 3,0,0 $	0	0	0	0	0	0	$-3\sqrt{6}e\epsilon\alpha_0$	0	0

where

$$\begin{aligned} \langle 3,2,1|\hat{H}_1|3,1,1\rangle &= -\frac{9}{2}e\epsilon\alpha_0, \langle 3,2,0|\hat{H}_1|3,1,0\rangle = -3\sqrt{3}e\epsilon\alpha_0, \langle 3,2,-1|\hat{H}_1|3,1,-1\rangle = -\frac{9}{2}e\epsilon\alpha_0, \\ \langle 3,1,0|\hat{H}_1|3,0,0\rangle &= -3\sqrt{6}e\epsilon\alpha_0. \end{aligned}$$

Note that

$$\hat{H}_1|3,2,2\rangle = 0, \quad \hat{H}_1|3,2,-2\rangle = 0$$

Thus $|3,2,2\rangle$ and $|3,2,-2\rangle$ are eigenstates of H_1 with the zero energy. So we consider the matrix under the basis $\{|3,2,1\rangle, |3,2,0\rangle, |3,2,-1\rangle, |3,1,1\rangle, |3,1,0\rangle, |3,1,-1\rangle, |3,0,0\rangle\}$.

	$ 3,2,1\rangle$	$ 3,2,0\rangle$	$ 3,2,-1\rangle$	$ 3,1,1\rangle$	$ 3,1,0\rangle$	$ 3,1,-1\rangle$	$ 3,0,0\rangle$
$\langle 3,2,1 $	0	0	0	$-\frac{9}{2}e\epsilon\alpha_0$	0	0	0
$\langle 3,2,0 $	0	0	0	0	$-3\sqrt{3}e\epsilon\alpha_0$	0	0
$\langle 3,2,-1 $	0	0	0	0	0	$-\frac{9}{2}e\epsilon\alpha_0$	0
$\langle 3,1,1 $	$-\frac{9}{2}e\epsilon\alpha_0$	0	0	0	0	0	0
$\langle 3,1,0 $	0	$-3\sqrt{3}e\epsilon\alpha_0$	0	0	0	0	$-3\sqrt{6}e\epsilon\alpha_0$
$\langle 3,1,-1 $	0	0	$-\frac{9}{2}e\epsilon\alpha_0$	0	0	0	0
$\langle 3,0,0 $	0	0	0	0	$-3\sqrt{6}e\epsilon\alpha_0$	0	0

This matrix consists of three submatrices.

(i)

	$ 3,2,0\rangle$	$ 3,1,0\rangle$	$ 3,0,0\rangle$
$\langle 3,2,0 $	0	$-3\sqrt{3}e\epsilon\alpha_0$	0
$\langle 3,1,0 $	$-3\sqrt{3}e\epsilon\alpha_0$	0	$-3\sqrt{6}e\epsilon\alpha_0$
$\langle 3,0,0 $	0	$-3\sqrt{6}e\epsilon\alpha_0$	0

or

$$M_1 = \begin{pmatrix} 0 & -3\sqrt{3}e\epsilon\alpha_0 & 0 \\ -3\sqrt{3}e\epsilon\alpha_0 & 0 & -3\sqrt{6}e\epsilon\alpha_0 \\ 0 & -3\sqrt{6}e\epsilon\alpha_0 & 0 \end{pmatrix}$$

Eigensystem[M_1] (Mathematica is used for the calculation)

$$E_1 = 9e\epsilon\alpha_0 = 3E_0 \quad |\psi_1\rangle = \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}|3,2,0\rangle - \sqrt{\frac{3}{2}}|3,1,0\rangle + |3,0,0\rangle\right]$$

$$E_2 = 0, \quad |\psi_2\rangle = \frac{1}{\sqrt{3}}[\sqrt{2}|3,2,0\rangle - |3,0,0\rangle]$$

$$E_3 = -9e\epsilon a_0 = -3E_0 \quad |\psi_3\rangle = \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}|3,2,0\rangle + \sqrt{\frac{3}{2}}|3,1,0\rangle + |3,0,0\rangle\right]$$

(ii)

$$\begin{array}{cc} & |3,2,-1\rangle & |3,1,-1\rangle \\ \langle 3,2,-1| & 0 & -\frac{9}{2}e\epsilon a_0 \\ \langle 3,1,-1| & -\frac{9}{2}e\epsilon a_0 & 0 \end{array}$$

$$M_2 = \begin{pmatrix} 0 & -\frac{9}{2}e\epsilon a_0 \\ -\frac{9}{2}e\epsilon a_0 & 0 \end{pmatrix}$$

Eigensystem[M_1] (Mathematica is used for the calculation)

$$\begin{array}{ll} E_4 = \frac{9}{2}e\epsilon a_0 = \frac{3}{2}E_0 & |\psi_4\rangle = \frac{1}{\sqrt{2}}[|3,2,-1\rangle - |3,1,-1\rangle] \\ E_5 = -\frac{9}{2}e\epsilon a_0 = -\frac{3}{2}E_0 & |\psi_5\rangle = \frac{1}{\sqrt{2}}[|3,2,-1\rangle + |3,1,-1\rangle] \end{array}$$

(iii)

$$\begin{array}{cc} & |3,2,1\rangle & |3,1,1\rangle \\ \langle 3,2,1| & 0 & -\frac{9}{2}e\epsilon a_0 \\ \langle 3,1,1| & -\frac{9}{2}e\epsilon a_0 & 0 \end{array}$$

$$M_3 = \begin{pmatrix} 0 & -\frac{9}{2}e\epsilon a_0 \\ -\frac{9}{2}e\epsilon a_0 & 0 \end{pmatrix}$$

Eigensystem[M_3] (Mathematica is used for the calculation)

$$\begin{array}{ll} E_4 = \frac{9}{2}e\epsilon a_0 = \frac{3}{2}E_0 & |\psi_6\rangle = \frac{1}{\sqrt{2}}[|3,2,1\rangle - |3,1,1\rangle] \\ E_5 = -\frac{9}{2}e\epsilon a_0 = -\frac{3}{2}E_0 & |\psi_7\rangle = \frac{1}{\sqrt{2}}[|3,2,1\rangle + |3,1,1\rangle] \end{array}$$

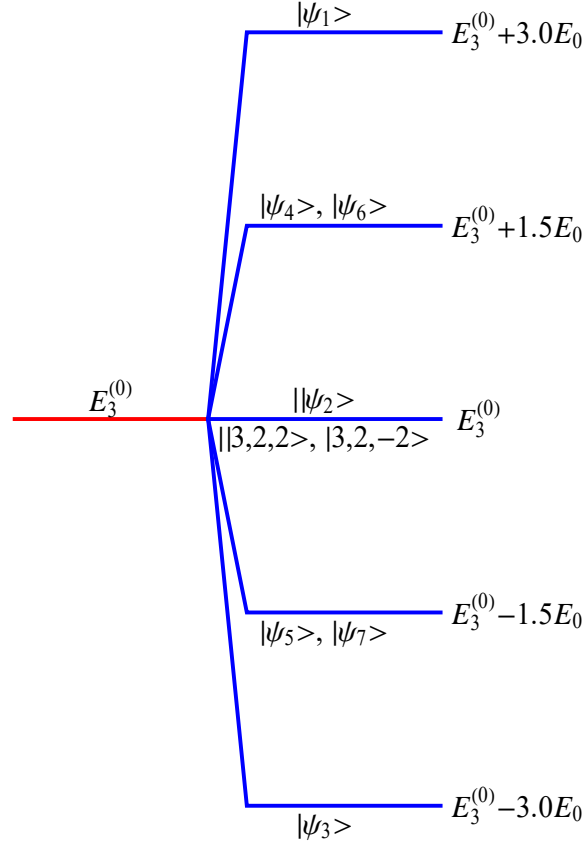


Fig. Energy splitting (Stark effect with $n = 3$). $E_0 = 3e\epsilon a_0$.

$$|\psi_1\rangle = \frac{1}{\sqrt{3}} \left[\frac{1}{\sqrt{2}} |3,2,0\rangle - \sqrt{\frac{3}{2}} |3,1,0\rangle + |3,0,0\rangle \right],$$

$$|\psi_2\rangle = \frac{1}{\sqrt{3}} \left[\sqrt{2} |3,2,0\rangle - |3,0,0\rangle \right],$$

$$|\psi_3\rangle = \frac{1}{\sqrt{3}} \left[\frac{1}{\sqrt{2}} |3,2,0\rangle + \sqrt{\frac{3}{2}} |3,1,0\rangle + |3,0,0\rangle \right],$$

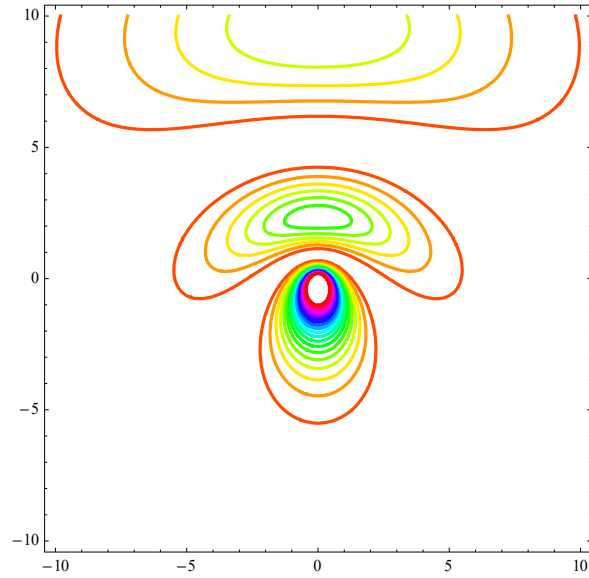
$$|\psi_4\rangle = \frac{1}{\sqrt{2}} \left[|3,2,-1\rangle - |3,1,-1\rangle \right],$$

$$|\psi_5\rangle = \frac{1}{\sqrt{2}} \left[|3,2,-1\rangle + |3,1,-1\rangle \right],$$

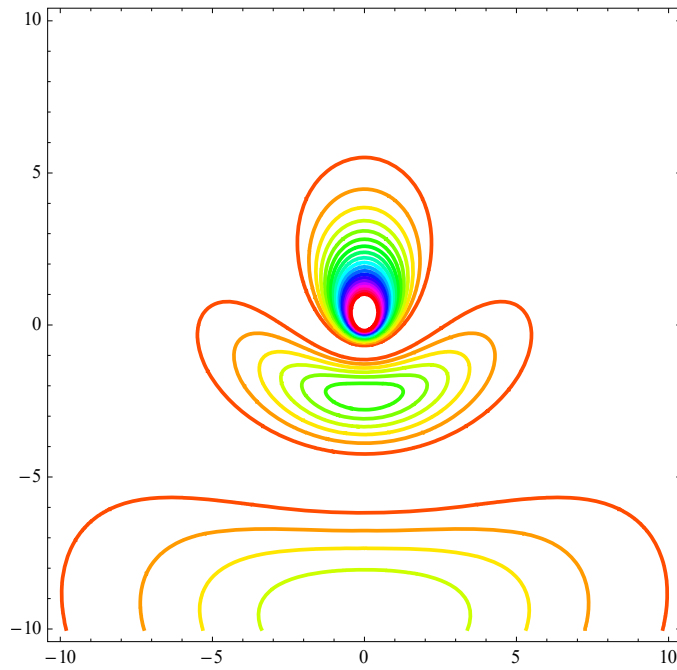
$$|\psi_6\rangle = \frac{1}{\sqrt{2}} \left[|3,2,1\rangle - |3,1,1\rangle \right]$$

$$|\psi_7\rangle = \frac{1}{\sqrt{2}} \left[|3,2,1\rangle + |3,1,1\rangle \right]$$

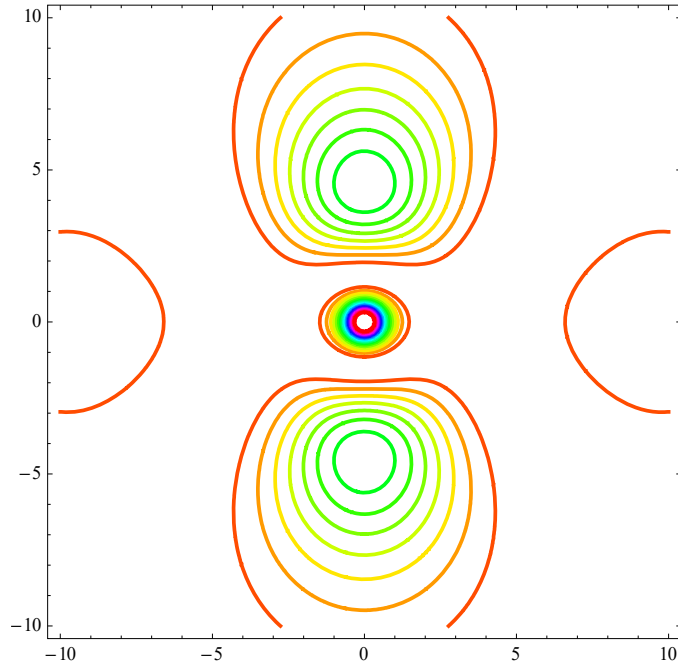
10 Charge density distribution for the Stark effect with $n = 3$



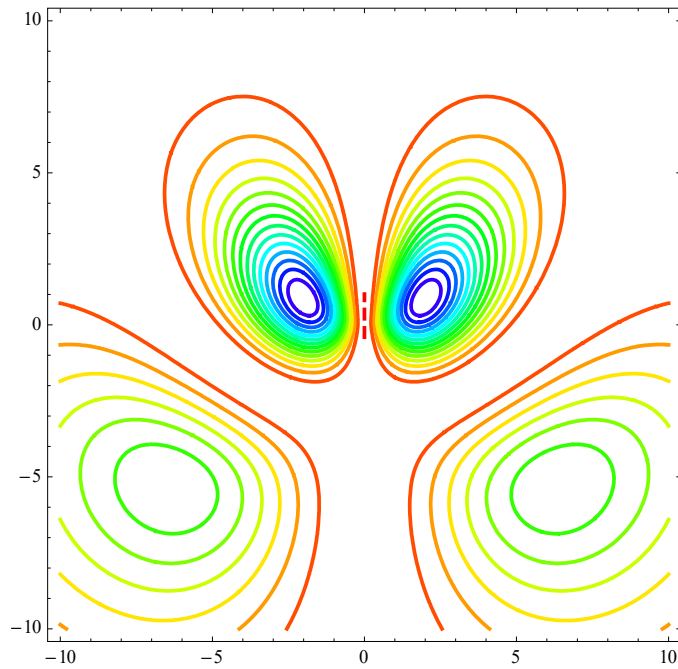
ContourPlot of $|\langle \mathbf{r} | \psi_1 \rangle|^2$ with $y=0$, in the x - z plane. The energy eigenvalue is $E_3^{(0)} + 3E_0$.



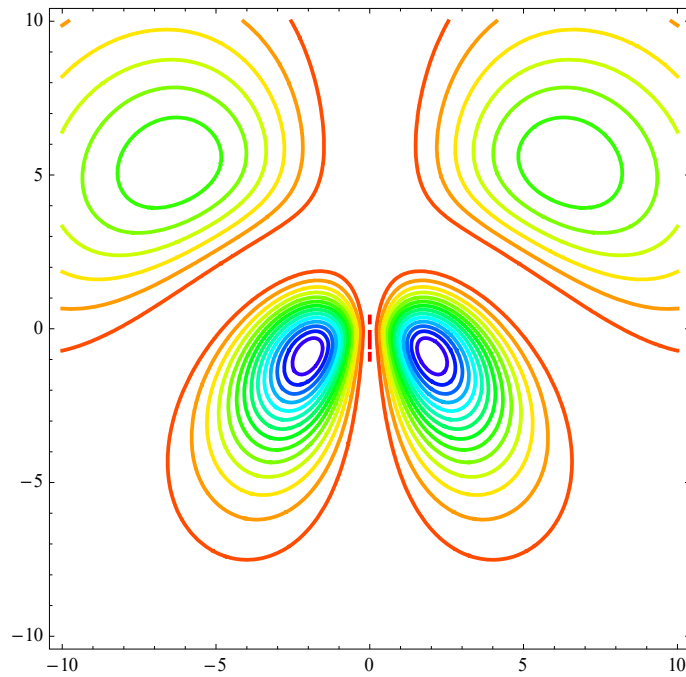
ContourPlot of $|\langle \mathbf{r} | \psi_3 \rangle|^2$ with $y=0$, in the x - z plane. The energy eigenvalue is $E_3^{(0)} - 3E_0$.



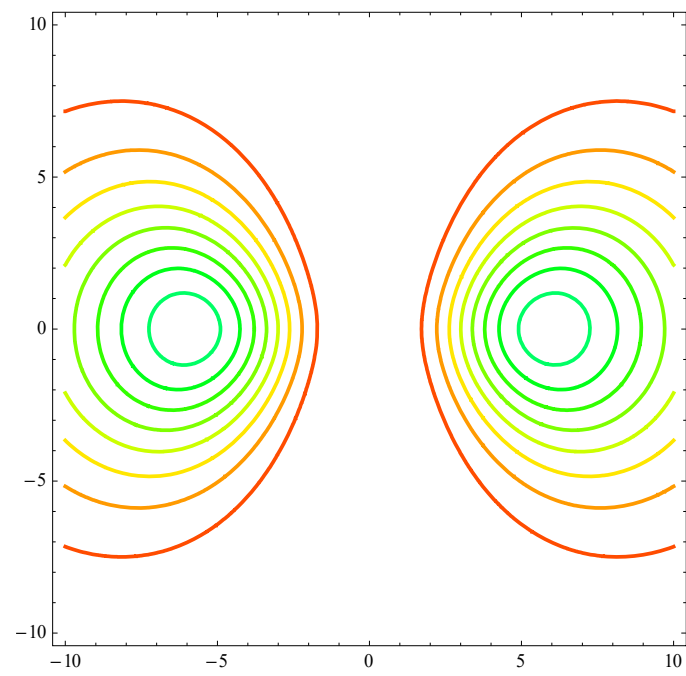
ContourPlot of $|\langle \mathbf{r} | \psi_2 \rangle|^2$ with $y=0$, in the x - z plane. The energy eigenvalue is $E_3^{(0)} - 3E_0$.



ContourPlot of $|\langle \mathbf{r} | \psi_7 \rangle|^2$ and $|\langle \mathbf{r} | \psi_5 \rangle|^2$ with $y=0$, in the x - z plane. The energy eigenvalue is $E_3^{(0)} - 1.5E_0$.



ContourPlot of $|\langle \mathbf{r} | \psi_6 \rangle|^2$ and $|\langle \mathbf{r} | \psi_4 \rangle|^2$ with $y=0$, in the x - z plane. The energy eigenvalue is $E_3^{(0)} + 1.5E_0$.



ContourPlot of $|\langle \mathbf{r} | 3,2,2 \rangle|^2$ and $|\langle \mathbf{r} | 3,2,-2 \rangle|^2$ with $y=0$, in the x - z plane. The energy eigenvalue is $E_3^{(0)}$.

11. Stark effect of hydrogen: energy levels for $n = 2$ and $n = 3$

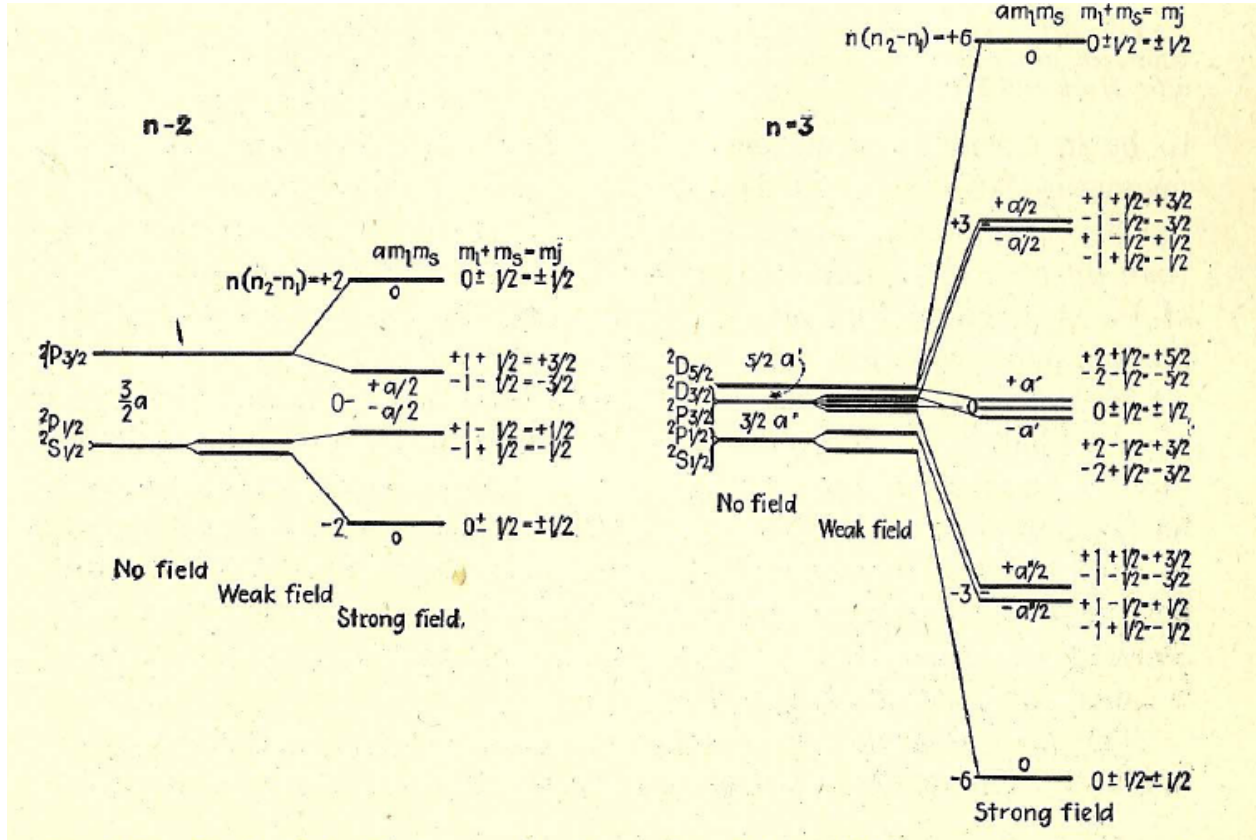


Fig. Stark effect of hydrogen, showing weak- and strong-field energy levels for $n = 2$ and $n = 3$. from the book of H. White, Introduction to Atomic Spectra (1934).

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- L.I. Schiff, Quantum Mechanics (McGraw-Hill, New York, 1995).
- H.A. Bethe and E.E. Salpeter, *Quantum Mechanics of One- and Two Electron Atoms*, Academic Press, New York, 1957, p.262]
- Stephen Gasiorowicz, *Quantum Physics*, 3rd edition (John Wiley & Sons, 2003).
- H. White, Introduction to Atomic Spectra (McGraw-Hill, 1934).

APPENDIX-I

The wavefunction of hydrogen atom:

$$\begin{aligned} \psi_{nlm}(r, \theta, \phi) &= \langle \mathbf{r} | n, l, m \rangle \\ &= \sqrt{\frac{(n-l-1)!}{(n+l)!}} 2^{1+l} a_0^{-l-3/2} \exp\left(-\frac{r}{na_0}\right) n^{-l-2} r^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta, \phi) \end{aligned}$$

The matrix element:

$$\langle n', l', m' | \hat{z} | n, l, m \rangle = \iiint r^2 \sin \theta dr d\theta d\phi \Omega \psi_{n'l'm'}^*(r, \theta, \phi) r \cos \theta \psi_{nlm}(r, \theta, \phi)$$

Calculation of matrix elements for $n = 3$

```

R[n_, l_, r_] :=
  1 / Sqrt[(n + l) !] (2^{1+l} a0^{-l-3/2} e^{-r/a0 n} n^{-l-2} r^l Sqrt[(n - l - 1) !] LaguerreL[-1 + n - l, 1 + 2 l, r/a0 n])
Y[l_, m_, theta_, phi_] := SphericalHarmonicY[l, m, theta, phi];
psi[n_, l_, m_, r_, theta_, phi_] := R[n, l, r] Y[l, m, theta, phi]
f[n1_, l1_, m1_, n2_, l2_, m2_, r_, theta_, phi_] =
  (-1)^{m1} psi[n1, l1, -m1, r, theta, phi] r Cos[theta] psi[n2, l2, m2, r, theta, phi] r^2 Sin[theta] // Simplify;
g[n1_, l1_, m1_, n2_, l2_, m2_] :=
  Integrate[Integrate[Integrate[f[n1, l1, m1, n2, l2, m2, r, theta, phi], {phi, 0, 2 pi}], {theta, 0, pi}],
    {r, 0, infinity} // Simplify;

```

Matrix element calculation

```

alpha = Simplify[g[3, 2, 1, 3, 1, 1], a0 > 0]; beta = Simplify[g[3, 2, 0, 3, 1, 0], a0 > 0];
gamma = Simplify[g[3, 2, -1, 3, 1, -1], a0 > 0];
delta = Simplify[g[3, 1, 0, 3, 0, 0], a0 > 0];

M1 = {{0, beta, 0}, {beta, 0, delta}, {0, delta, 0}}
{{0, -3 Sqrt[3] a0, 0}, {-3 Sqrt[3] a0, 0, -3 Sqrt[6] a0}, {0, -3 Sqrt[6] a0, 0}}

eq1 = Eigensystem[M1]
{{0, -9 a0, 9 a0}, {{-Sqrt[2], 0, 1}, {1/Sqrt[2], Sqrt[3/2], 1}, {1/Sqrt[2], -Sqrt[3/2], 1}}}

M2 = {{0, alpha}, {alpha, 0}}
{{0, -9 a0/2}, {-9 a0/2, 0}}

eq2 = Eigensystem[M2] // Simplify
{{-9 a0/2, 9 a0/2}, {{1, 1}, {-1, 1}}}

M3 = {{0, alpha}, {alpha, 0}}
{{0, -9 a0/2}, {-9 a0/2, 0}}

Eigensystem[M3]
{{-9 a0/2, 9 a0/2}, {{1, 1}, {-1, 1}}}

```

APPENDIX-II Polarizability

F: force,

$$F = qE \quad [\text{dyne} = \text{erg/cm}],$$

where q is the charge. The polarization P is

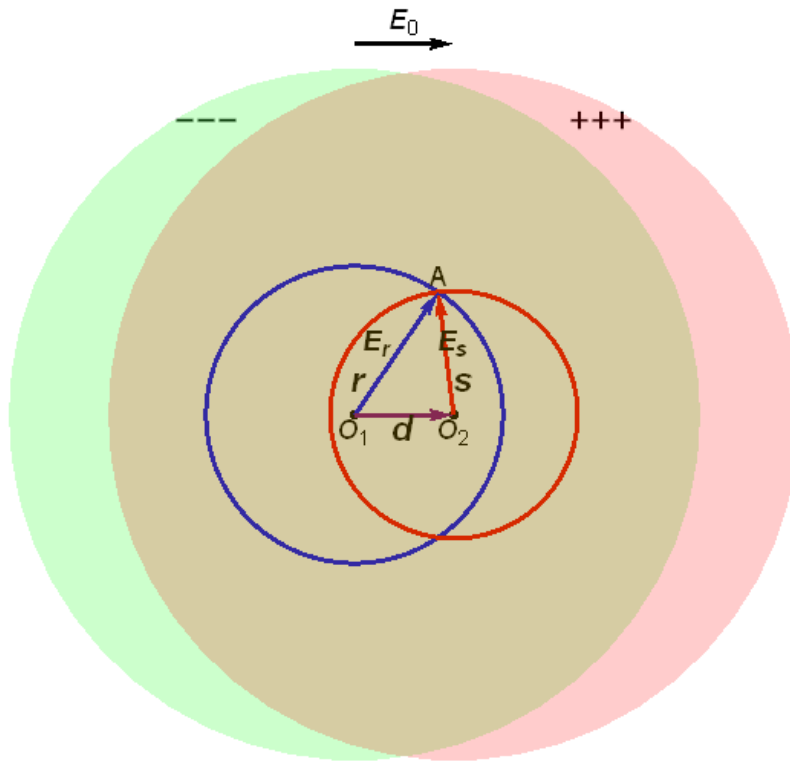
$$p = \alpha E = qr.$$

Then we get

$$\alpha = \frac{qr}{E} = \frac{q^2 r}{qE} = \left[\frac{\text{erg} \cdot \text{cm}^2}{\text{erg/cm}} \right] = [\text{cm}^3].$$

We have two spheres, each of radius a , one of which has volume charge density $+\rho$ and the other of which has density $-\rho$. The vector from the center of the positive sphere to the center of the negative sphere is d . The two spheres have a region of overlap and we want the electric field within this region.

Suppose that an external electric field (E_0) is applied to a dielectric sphere. As a result, there occurs a polarization inside the sphere. For simplicity, we consider a positive charged sphere (the charge density ρ) centered at the point O_2 , and a negative charged sphere (the charge density $-\rho$) centered at the point O_1 . The point O_2 is deviated from the point O_1 by a vector d . The overlapped region has no charge because of the cancellation of charges. The positive charges appear at the pink region (the right edge) and the negative charges appear at the green region (the left edge).



We see that the electric field inside a uniformly negatively charged sphere is (restoring the vector notation)

$$E_r = \frac{4\pi}{4\pi r^2} \frac{4\pi r^3(-\rho)}{3} = -\frac{4\pi\rho}{3} r,$$

or

$$E_r = -\frac{4\pi\rho}{3} \mathbf{r}$$

where \mathbf{r} is the vector from the center of the sphere (O_1) to the point in question (A). Now suppose that \mathbf{s} is the vector from the center of the positive sphere to the same point. So we get

$$E_s = \frac{4\pi\rho}{3} \mathbf{s}$$

So the total electric field is, using the superposition

$$E' = E_r + E_s = \frac{4\pi\rho}{3}(\mathbf{r} - \mathbf{s}) = -\frac{4\pi\rho}{3} \mathbf{d} = -\frac{4\pi}{3} \mathbf{P}$$

where $\mathbf{r} - \mathbf{s} = -\mathbf{d}$. The resultant electric field inside the sphere is

$$E_i = E_0 + E' = E_0 - \frac{4\pi}{3} \mathbf{P}$$

The polarization vector is defined by

$$\mathbf{P} = \rho \mathbf{d}$$

The electric field due to the polarization vector is $-\frac{4\pi}{3} \mathbf{P}$.

For the system (sphere, radius R) with the total charge q , the charge density ρ is obtained as

$$q = \frac{4\pi R^3}{3} \rho$$

Then we have

$$E = \frac{4\pi}{3} d \frac{3q}{4\pi R^3} = \frac{qd}{R^3} = \frac{p}{R^3}$$

or

$$p = R^3 E = \alpha E$$

The polarizability is given by

$$\alpha = R^3.$$

For the hydrogen, if we take $R = a_0 = 0.52917721092 \text{ \AA}$, we get

$$\alpha = a_0^3 = 1.48185 \times 10^{-25} \text{ cm}^3.$$