Chapter 41S
Stark effect in hydrogen

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41S.1 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.

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

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

where $-e$ (e>0) is the electron charge and $\boldsymbol{\mu}_e$ (=-e**r**) is an electric dipole moment. The vector **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.

41S.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

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

unless $l' = l \pm 1$.

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 (see Chapter 27 for the notation).

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

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

or

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

or

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

or

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

Since

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

We have

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

or

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

Since

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

we have

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

((**Note-1**)) $[\hat{L}_z,\hat{z}] = 0$

Using this relation we calculate the matrix element;

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

Thus

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

((**Note-2**)) $\hat{L}^4\hat{z} - 2\hat{L}^2\hat{z}\hat{L}^2 + \hat{z}\hat{L}^4 - 2\hbar^2(\hat{L}^2\hat{z} + \hat{z}\hat{L}^2) = 0$.

Using this relation we can calculate the matrix element;

$$\langle n,l,m|\hat{L}^4\hat{z} - 2\hat{L}^2\hat{z}\hat{L}^2 + \hat{z}\hat{L}^4 - 2\hbar^2(\hat{L}^2\hat{z} + \hat{z}\hat{L}^2)|n',l',m'\rangle = 0.$$

This expression yields

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

Then we have

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

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

((**Note-3**)) $\hat{\pi}$ 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

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

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

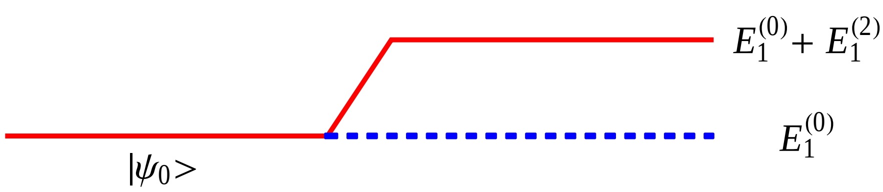
When $l+l'+1 = 2k+1$ (odd numbers), or $l+l' = 2k$ (even number), we have

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

41S.3 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

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

Then we have

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

or

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

The proceeding 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.

41S.4 Polarizability of the 1s-state

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

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

or

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

Under the perturbation, the energy shift is given by

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

((**Note-1**))

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

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

The electric field ε causes an induced dipole moment to appear, proportional to ε.

((**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

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

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

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

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

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

which is consistent with the experimentally observed value: $\alpha = 4.5\ a_0^3$.

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

((**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?

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

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

Here

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

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

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

Then we have

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

or

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

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]

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

$$E_n=-\frac{m_0e^4}{2n^2\hbar^2}=-\frac{e^2}{2n^2a_0}$$

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

Then we have

$$\alpha=2e^2\sum_{n\neq1}\frac{|\langle n,1,0|\hat{z}|1,0,0\rangle|^2}{E_n{}^{(0)}-E_1{}^{(0)}}=4a_0{}^3\sum_{n=2}^\infty\frac{n^2f(n)}{n^2-1}=4a_0{}^3 0.915806=3.66326a_0{}^3$$

((**Mathematica**))

Stark effect with n = 1

```
Clear["Global`*"];
R[n_, ℓ_, r_] := 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, (2 r)/(a0 n)]);
Y[ℓ_, m_, θ_, ϕ_] := SphericalHarmonicY[ℓ, m, θ, ϕ];
ψ[n_, ℓ_, m_, r_, θ_, ϕ_] := R[n, ℓ, r] Y[ℓ, m, θ, ϕ]
f[n1_, ℓ1_, m1_, n2_, ℓ2_, m2_, r_, θ_, ϕ_] =
  (-1)^m1 ψ[n1, ℓ1, -m1, r, θ, ϕ] r Cos[θ] ψ[n2, ℓ2, m2, r, θ, ϕ] r^2 Sin[θ] // Simplify;
```

Integral calculation

```
g[n1_, ℓ1_, m1_, n2_, ℓ2_, m2_] :=
 Simplify[Integrate[Integrate[Integrate[f[n1, ℓ1, m1, n2, ℓ2, m2, r, θ, ϕ]/a0, {ϕ, 0, 2 π}],
    {θ, 0, π}], {r, 0, ∞}], a0 > 0];
```

Beth' s formula

```
h[n_] = 1/3 (2^8 n^7 (n - 1)^(2 n-5))/((n + 1)^(2 n+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

41S.5 Stark effect on the n = 2 level

We now consider the state with n = 2.

n = 2 state (4 states-degeneracy):

l = 1 (m = ±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

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

$$\left|\psi_2^{(0)}\right\rangle = \left|2,1,1\right\rangle$$
$$\left|\psi_3^{(0)}\right\rangle = \left|2,1,0\right\rangle \qquad \text{odd states}$$
$$\left|\psi_4^{(0)}\right\rangle = \left|2,1,-1\right\rangle$$

From the selection rule, we have

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

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

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

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

$$(\hat{H}_1)_{13} = e\varepsilon\left\langle\psi_3^{(0)}\right|\hat{z}\left|\psi_1^{(0)}\right\rangle = -3e\varepsilon a_0 = -E_0$$

or

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

Note that

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

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

	$\|2,1,1\rangle$	$\|2,1,0\rangle$	$\|2,1,-1\rangle$	$\|2,0,0\rangle$
$\langle 2,1,1\|$	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

where

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

The reduced matrix:

	$\|2,1,0\rangle$	$\|2,0,0\rangle$
$\langle 2,1,0\|$	0	$-E_0$
$\langle 2,0,0\|$	$-E_0$	0

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 λ = -E_0 (the lowest level)

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

For λ = E_0, (the highest level)

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

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

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

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

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

$\left|\psi_2^{(0)}\right\rangle$ and $\left|\psi_4^{(0)}\right\rangle$

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

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

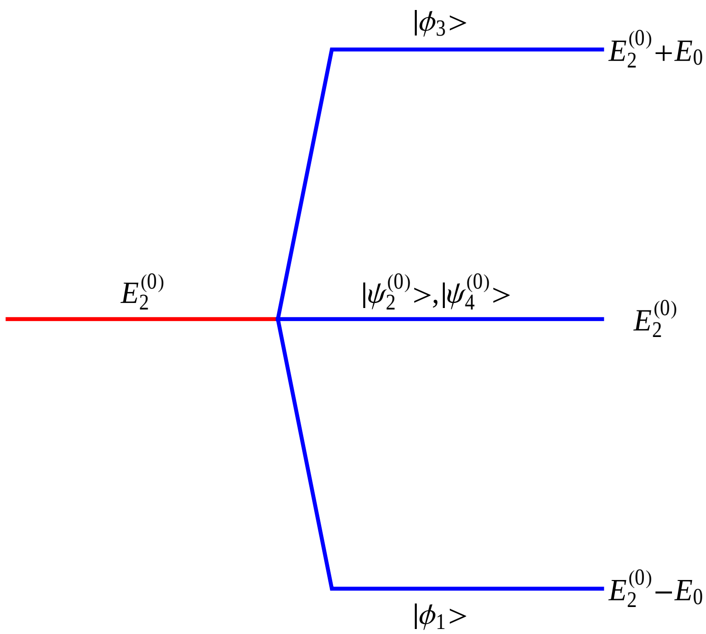


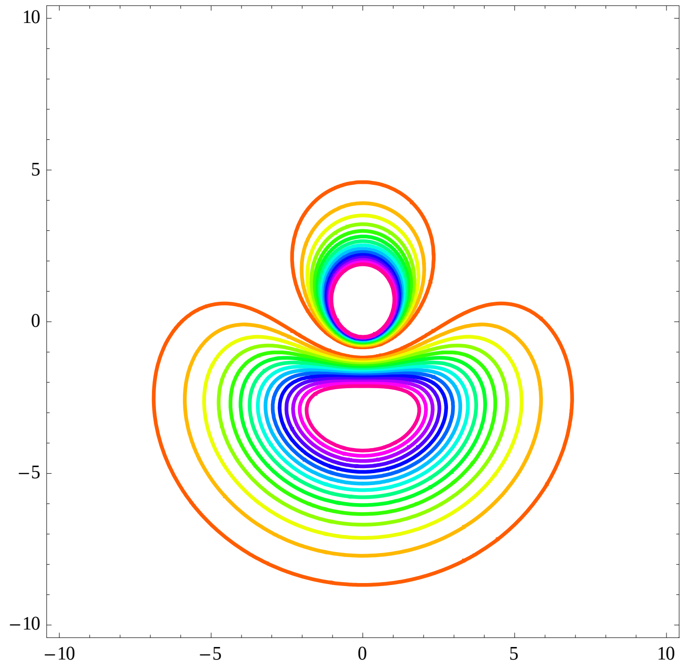
Fig. Energy splitting (Stark effect with n = 2). $E_0 = 3e\varepsilon a_0$.

41S.6 Charge density distribution for the Stark effect with *n* = 2

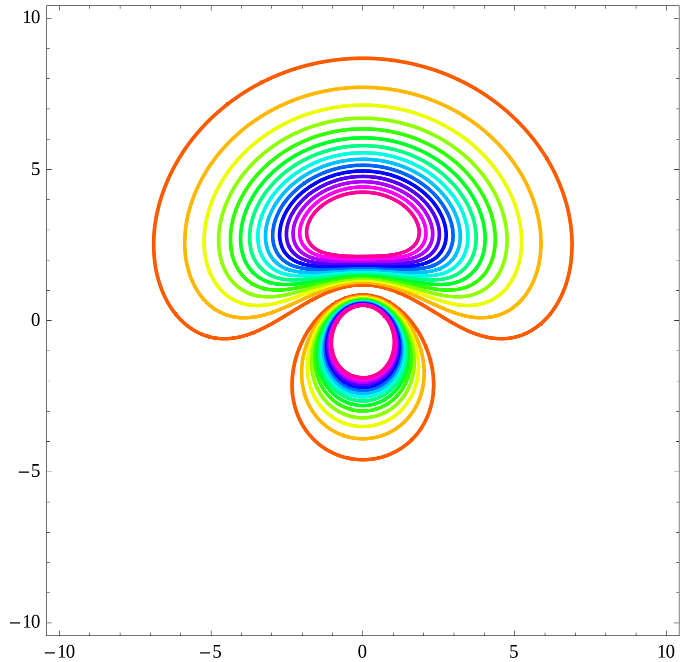
The charge density distribution for the $|\varphi_1\rangle$, $|\varphi_3\rangle$, $|\psi_2{}^{(0)}\rangle$ and $|\psi_4{}^{(0)}\rangle$ is evaluated from the CountourPlot (Mathematica) of

$$|\langle \mathbf{r}|\varphi_1\rangle|^2, \quad |\langle \mathbf{r}|\varphi_3\rangle|^2, \ |\langle \mathbf{r}|\psi_2{}^{(0)}\rangle|^2, \text{ and } |\langle \mathbf{r}|\psi_4{}^{(0)}\rangle|^2$$

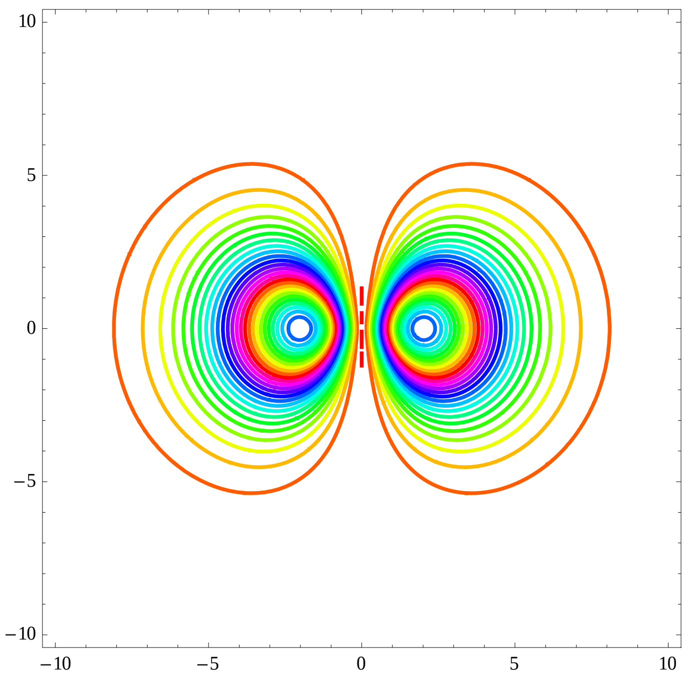
where y = 0, in the x-z plane.



ContourPlot of $\left|\langle \mathbf{r}|\varphi_1\rangle\right|^2$ 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 $\left|\langle \mathbf{r}|\varphi_3\rangle\right|^2$ 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 $\left|\langle \mathbf{r}|\psi_2^{(0)}\rangle\right|^2 = \left|\langle \mathbf{r}|\psi_4^{(0)}\rangle\right|^2$ 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

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

and

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

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)!]
   (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, (2 r)/(a0 n)])
Y[ℓ_, m_, θ_, ϕ_] := SphericalHarmonicY[ℓ, m, θ, ϕ];
ψ[n_, ℓ_, m_, r_, θ_, ϕ_] := R[n, ℓ, r] Y[ℓ, m, θ, ϕ];
f[n1_, ℓ1_, m1_, n2_, ℓ2_, m2_, r_, θ_, ϕ_] =
  (-1)^m1 ψ[n1, ℓ1, -m1, r, θ, ϕ] r Cos[θ] ψ[n2, ℓ2, m2, r, θ, ϕ]
    r^2 Sin[θ] // Simplify;

Simplify[
 Integrate[
  Integrate[Integrate[f[2, 1, 0, 2, 0, 0, r, θ, ϕ],
    {ϕ, 0, 2 π}], {θ, 0, π}], {r, 0, ∞}], a0 > 0]
```

$-3\,a0$

E0 = 3 e a0 ε; Eigenvalue problem for the simplified system

H22 = {{0, -E0}, {-E0, 0}}

{{0, -E0}, {-E0, 0}}

eq1 = Eigensystem[H22]

{{-E0, E0}, {{1, 1}, {-1, 1}}}

ψ1 = Normalize[eq1[[2, 1]]]

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

ψ2 = -Normalize[eq1[[2, 2]]]

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

UT = {ψ1, ψ2}

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

U = Transpose[UT]

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

UH = UT

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

UH.U

{{1, 0}, {0, 1}}

41S.7 n = 3 Stark effect

We consider the case of $n = 3$.

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

$l = 2$ ($m = \pm 2, \pm 1, 0$):	d-state (5 states)
$l = 1$ ($m = \pm 1, 0$):	p-state 3 states)
$l = 0$ ($m = 0$):	s-state (1 state)

Note that

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

is the eigenvalue of $\hat{H}_0$.

Matrix elements of H_1:

	$\lvert 3,2,2\rangle$	$\lvert 3,2,1\rangle$	$\lvert 3,2,0\rangle$	$\lvert 3,2,-1\rangle$	$\lvert 3,2,-2\rangle$	$\lvert 3,1,1\rangle$	$\lvert 3,1,0\rangle$	$\lvert 3,1,-1\rangle$	$\lvert 3,0,0\rangle$
$\langle 3,2,2\rvert$	0	0	0	0	0	0	0	0	0
$\langle 3,2,1\rvert$	0	0	0	0	0	$-\frac{9}{2}e\varepsilon a_0$	0	0	0
$\langle 3,2,0\rvert$	0	0	0	0	0	0	$-3\sqrt{3}e\varepsilon a_0$	0	0
$\langle 3,2,-1\rvert$	0	0	0	0	0	0	0	$-\frac{9}{2}e\varepsilon a_0$	0
$\langle 3,2,-2\rvert$	0	0	0	0	0	0	0	0	0
$\langle 3,1,1\rvert$	0	$-\frac{9}{2}e\varepsilon a_0$	0	0	0	0	0	0	0
$\langle 3,1,0\rvert$	0	0	$-3\sqrt{3}e\varepsilon a_0$	0	0	0	0	0	$-3\sqrt{6}e\varepsilon a_0$
$\langle 3,1,-1\rvert$	0	0	0	$-\frac{9}{2}e\varepsilon a_0$	0	0	0	0	0
$\langle 3,0,0\rvert$	0	0	0	0	0	0	$-3\sqrt{6}e\varepsilon a_0$	0	0

where

$$\langle 3,2,1|\hat{H}_1|3,1,1\rangle = -\frac{9}{2}e\varepsilon a_0, \langle 3,2,0|\hat{H}_1|3,1,0\rangle = -3\sqrt{3}e\varepsilon a_0, \langle 3,2,-1|\hat{z}|3,1,-1\rangle = -\frac{9}{2}e\varepsilon a_0,$$
$$\langle 3,1,0|\hat{z}|3,0,0\rangle = -3\sqrt{6}e\varepsilon a_0.$$

Note that

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

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	$-\frac{9}{2}e\varepsilon a_0$	0	0	0
$\langle 3,2,0\|$	0	0	0	0	$-3\sqrt{3}e\varepsilon a_0$	0	0
$\langle 3,2,-1\|$	0	0	0	0	0	$-\frac{9}{2}e\varepsilon a_0$	0
$\langle 3,1,1\|$	$-\frac{9}{2}e\varepsilon a_0$	0	0	0	0	0	0
$\langle 3,1,0\|$	0	$-3\sqrt{3}e\varepsilon a_0$	0	0	0	0	$-3\sqrt{6}e\varepsilon a_0$
$\langle 3,1,-1\|$	0	0	$-\frac{9}{2}e\varepsilon a_0$	0	0	0	0
$\langle 3,0,0\|$	0	0	0	0	$-3\sqrt{6}e\varepsilon a_0$	0	0

This matrix consists of three submnatrices.

(i)

	$\|3,2,0\rangle$	$\|3,1,0\rangle$	$\|3,0,0\rangle$
$\langle 3,2,0\|$	0	$-3\sqrt{3}e\varepsilon a_0$	0
$\langle 3,1,0\|$	$-3\sqrt{3}e\varepsilon a_0$	0	$-3\sqrt{6}e\varepsilon a_0$
$\langle 3,0,0\|$	0	$-3\sqrt{6}e\varepsilon a_0$	0

or

$$M_1 = \begin{pmatrix} 0 & -3\sqrt{3}e\varepsilon a_0 & 0 \\ -3\sqrt{3}e\varepsilon a_0 & 0 & -3\sqrt{6}e\varepsilon a_0 \\ 0 & -3\sqrt{6}e\varepsilon a_0 & 0 \end{pmatrix}$$

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

$E_1 = 9e\varepsilon a_0 = 3E_0 \qquad |\psi_1\rangle = \frac{1}{\sqrt{3}}[\frac{1}{\sqrt{2}}|3,2,0\rangle - \sqrt{\frac{3}{2}}|3,1,0\rangle + |3,0,0\rangle]$

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

E_3 = -9eεa$_0$ = -3E_0 $\quad |\psi_3\rangle = \frac{1}{\sqrt{3}}[\frac{1}{\sqrt{2}}|3,2,0\rangle + \sqrt{\frac{3}{2}}|3,1,0\rangle + |3,0,0\rangle]$

(ii)

	$\|3,2,-1\rangle$	$\|3,1,-1\rangle$
$\langle 3,2,-1\|$	0	$-\frac{9}{2}e\varepsilon a_0$
$\langle 3,1,-1\|$	$-\frac{9}{2}e\varepsilon a_0$	0

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

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

E_4 = $\frac{9}{2}$ eεa$_0$ = $\frac{3}{2}$ E_0 $\quad |\psi_4\rangle = \frac{1}{\sqrt{2}}[|3,2,-1\rangle - |3,1,-1\rangle]$

E_5 = -$\frac{9}{2}$ eεa$_0$= -$\frac{3}{2}$ E_0 $\quad |\psi_5\rangle = \frac{1}{\sqrt{2}}[[|3,2,-1\rangle + |3,1,-1\rangle]]$

(iii)

	$\|3,2,1\rangle$	$\|3,1,1\rangle$
$\langle 3,2,1\|$	0	$-\frac{9}{2}e\varepsilon a_0$
$\langle 3,1,1\|$	$-\frac{9}{2}e\varepsilon a_0$	0

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

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

E_4 = $\frac{9}{2}$ eεa$_0$ = $\frac{3}{2}$ E_0 $\quad |\psi_6\rangle = \frac{1}{\sqrt{2}}[|3,2,1\rangle - |3,1,1\rangle]$

E_5 = -$\frac{9}{2}$ eεa$_0$ = -$\frac{3}{2}$ E_0 $\quad |\psi_7\rangle = \frac{1}{\sqrt{2}}[[|3,2,1\rangle + |3,1,1\rangle]]$

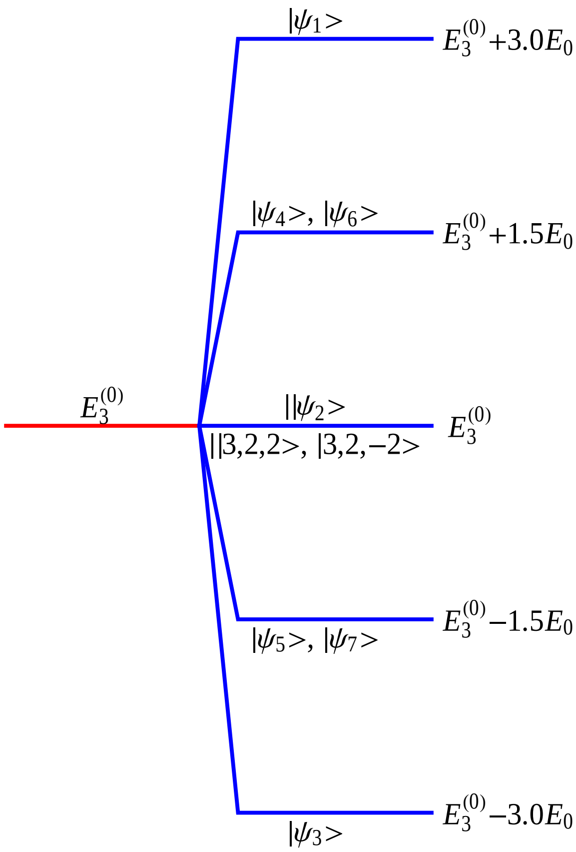
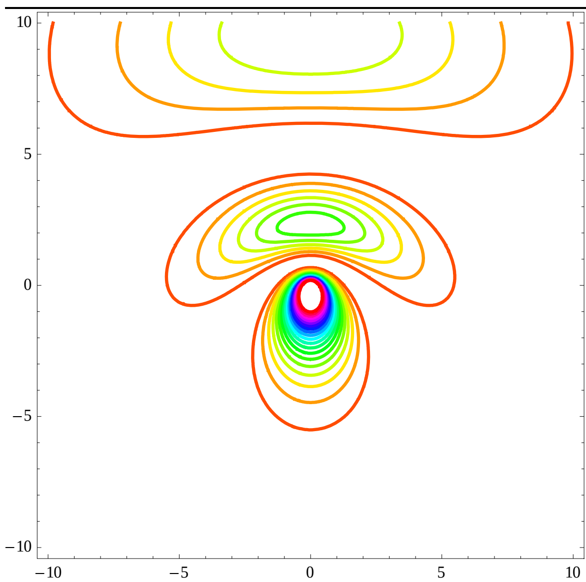
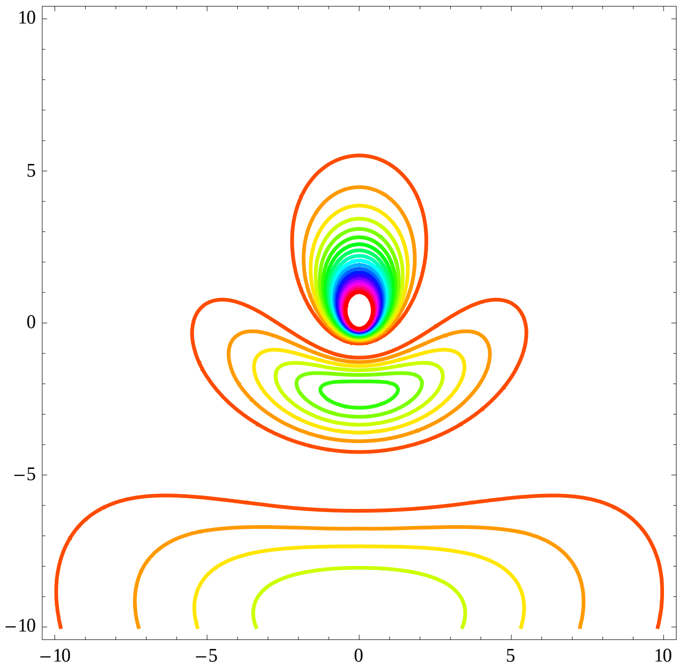


Fig. Energy splitting (Stark effect with n = 3). $E_0 = 3e\varepsilon a_0$.

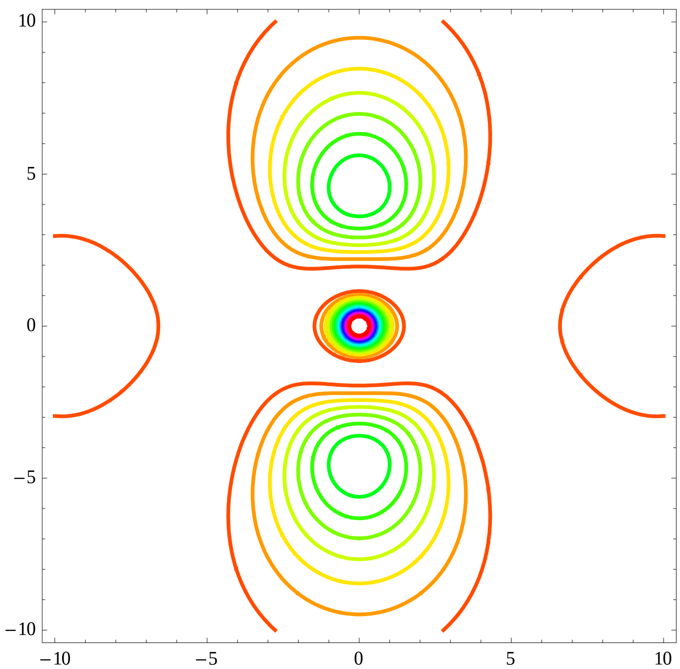
41S.8 Charge density distribution for the Stark effect with *n* = 3



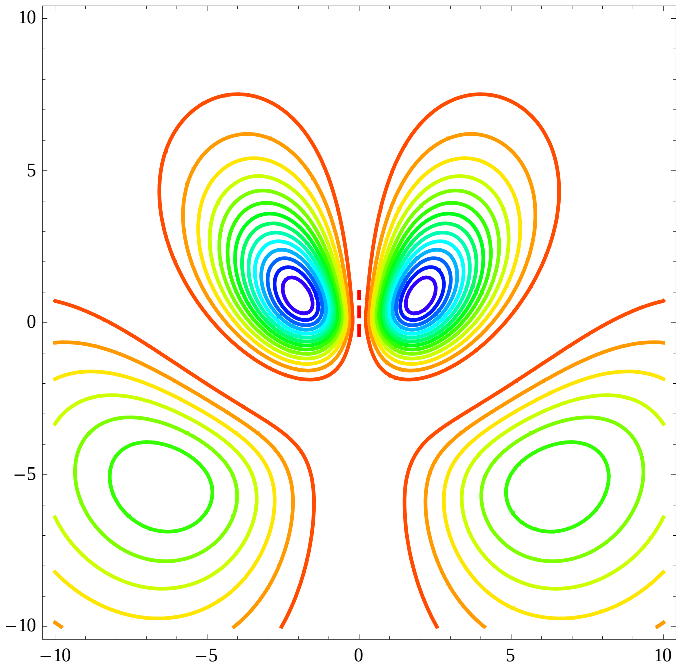
ContourPlot of $\left|\langle \mathbf{r}|\psi_1\rangle\right|^2$ with y =0, in the x-z plane. The energy eigenvalue is $E_3^{(0)} + 3E_0$.



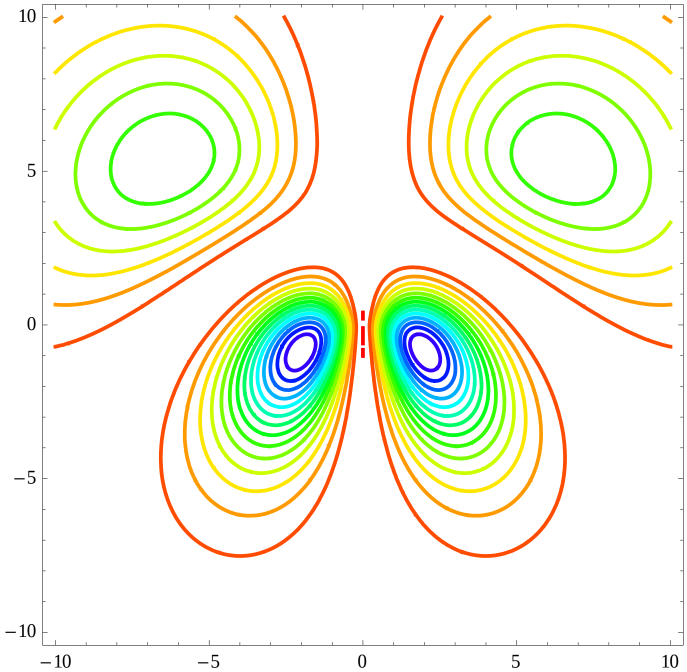
ContourPlot of $\left|\langle \mathbf{r}|\psi_3\rangle\right|^2$ with $y=0$, in the x-z plane. The energy eigenvalue is $E_3^{(0)}-3E_0$.



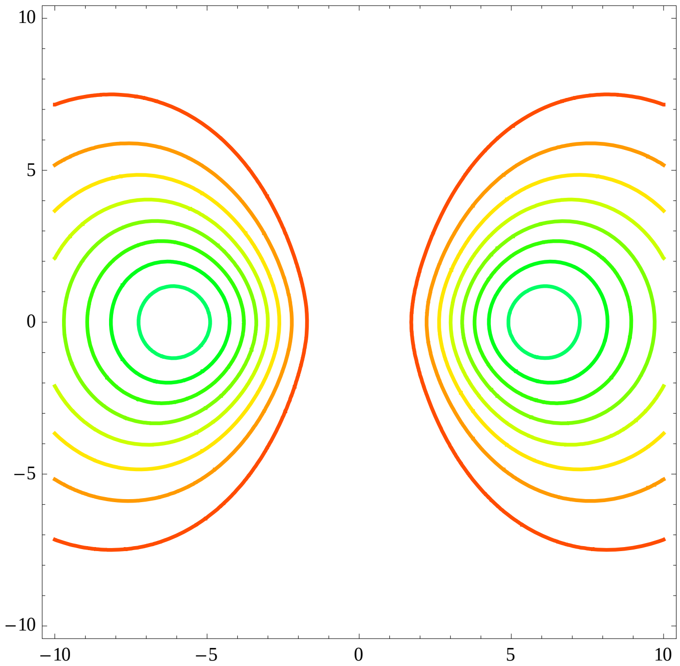
ContourPlot of $\left|\langle \mathbf{r}|\psi_2\rangle\right|^2$ with $y=0$, in the x-z plane. The energy eigenvalue is $E_3^{(0)}-3E_0$.



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



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



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

REFERENCES

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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).

APPENDIX

The wavefunction of hydrogen atom:

$$\psi_{nlm}(r,\theta,\phi) = \langle \mathbf{r} | n,l,m\rangle$$
$$= \sqrt{\frac{(n-l-1)!}{(n+l)!}} 2^{1+l} a_0^{-l-3/2} \exp(-\frac{r}{na0}) n^{-l-2} r^l L_{n-l-1}^{2l+1}(\frac{2r}{na_0}) Y_l^m(\theta,\phi)$$

The matrix element:

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

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, (2 r)/(a0 n)])

Y[ℓ_, m_, θ_, ϕ_] := SphericalHarmonicY[ℓ, m, θ, ϕ];
ψ[n_, ℓ_, m_, r_, θ_, ϕ_] := R[n, ℓ, r] Y[ℓ, m, θ, ϕ]

f[n1_, ℓ1_, m1_, n2_, ℓ2_, m2_, r_, θ_, ϕ_] =
 (-1)^m1 ψ[n1, ℓ1, -m1, r, θ, ϕ] r Cos[θ] ψ[n2, ℓ2, m2, r, θ, ϕ] r^2 Sin[θ] // Simplify;
g[n1_, ℓ1_, m1_, n2_, ℓ2_, m2_] :=
 Integrate[Integrate[Integrate[f[n1, ℓ1, m1, n2, ℓ2, m2, r, θ, ϕ], {ϕ, 0, 2 π}], {θ, 0, π}],
   {r, 0, ∞}] // Simplify;
```

Matrix element calculation

```
α = Simplify[g[3, 2, 1, 3, 1, 1], a0 > 0]; β = Simplify[g[3, 2, 0, 3, 1, 0], a0 > 0];
γ = Simplify[g[3, 2, -1, 3, 1, -1], a0 > 0];
δ = Simplify[g[3, 1, 0, 3, 0, 0], a0 > 0];

M1 = {{0, β, 0}, {β, 0, δ}, {0, δ, 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]
```

$$\left\{\{0, -9\,a0, 9\,a0\}, \left\{\{-\sqrt{2}, 0, 1\}, \left\{\frac{1}{\sqrt{2}}, \sqrt{\frac{3}{2}}, 1\right\}, \left\{\frac{1}{\sqrt{2}}, -\sqrt{\frac{3}{2}}, 1\right\}\right\}\right\}$$

```
M2 = {{0, α}, {α, 0}}
```

$$\left\{\left\{0, -\frac{9\,a0}{2}\right\}, \left\{-\frac{9\,a0}{2}, 0\right\}\right\}$$

```
eq2 = Eigensystem[M2] // Simplify
```

$$\left\{\left\{-\frac{9\,a0}{2}, \frac{9\,a0}{2}\right\}, \{\{1, 1\}, \{-1, 1\}\}\right\}$$

```
M3 = {{0, α}, {α, 0}}
```

$$\left\{\left\{0, -\frac{9\,a0}{2}\right\}, \left\{-\frac{9\,a0}{2}, 0\right\}\right\}$$

```
Eigensystem[M3]
```

$$\left\{\left\{-\frac{9\,a0}{2}, \frac{9\,a0}{2}\right\}, \{\{1, 1\}, \{-1, 1\}\}\right\}$$