# The Stark Effect

*Grading:* Each part is worth 10 points, but part (d) is optional.

**a. Evaluate a matrix element.**

$$\begin{aligned}
\langle 200|H'|210\rangle &= eE\langle 200|z|210\rangle \\
&= eE\langle 200|r\cos\theta|210\rangle \\
&= eE\int_0^\infty r^2\,dr\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi} d\phi\; R_{20}^*(r)Y_0^{0*}(\theta,\phi)\,r\cos\theta\,R_{21}(r)Y_1^0(\theta,\phi)
\end{aligned}$$

**Angular part** — use Griffiths page 139 for $Y_\ell^m(\theta,\phi)$

$$\begin{aligned}
\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi} d\phi\; Y_0^{0*}(\theta,\phi)\,\cos\theta\,Y_1^0(\theta,\phi) &= \int_0^\pi \sin\theta\,d\theta\int_0^{2\pi} d\phi\left[\sqrt{\frac{1}{4\pi}}\right]\cos\theta\left[\sqrt{\frac{3}{4\pi}}\cos\theta\right] \\
&= \frac{\sqrt{3}}{4\pi}(2\pi)\int_0^\pi \sin\theta\,d\theta\,\cos^2\theta
\end{aligned}$$

Use the famous substitution

$$\begin{aligned}
\mu &= \cos\theta \\
d\mu &= -\sin\theta\,d\theta
\end{aligned}$$

to find that the angular part is

$$\begin{aligned}
\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi} d\phi\; Y_0^{0*}(\theta,\phi)\,\cos\theta\,Y_1^0(\theta,\phi) &= \frac{\sqrt{3}}{2}\int_{-1}^{+1}\mu^2\,d\mu \\
&= \sqrt{3}\int_0^1 \mu^2\,d\mu = \frac{\sqrt{3}}{3}\left[\mu^3\right]_0^1 = \frac{1}{\sqrt{3}}
\end{aligned}$$

**Radial part** — use Griffiths page 154 for $R_{20}(r)$ and $R_{21}(r)$:

$$\int_0^\infty r^2\,dr\,R_{20}^*(r)\,r\,R_{21}(r) = \int_0^\infty r^2\,dr\left[\frac{1}{\sqrt{2}}a_0^{-3/2}\left(1-\frac{1}{2}\frac{r}{a_0}\right)e^{-(r/a_0)/2}\right]r\left[\frac{1}{\sqrt{24}}a_0^{-3/2}\left(\frac{r}{a_0}\right)e^{-(r/a_0)/2}\right]$$

Use the substitution $\tilde{r} = r/a_0$:

$$\begin{aligned}
\int_0^\infty r^2\,dr\,R_{20}^*(r)\,r\,R_{21}(r) &= \frac{a_0}{4\sqrt{3}}\int_0^\infty \tilde{r}^4\,d\tilde{r}\left(1-\frac{1}{2}\tilde{r}\right)e^{-\tilde{r}} \\
&= \frac{a_0}{4\sqrt{3}}\left[\int_0^\infty d\tilde{r}\,\tilde{r}^4 e^{-\tilde{r}} - \frac{1}{2}\int_0^\infty d\tilde{r}\,\tilde{r}^5 e^{-\tilde{r}}\right]
\end{aligned}$$

According to Dwight 860.07 these two integrals evaluate to $4! = 24$ and to $5! = 120$ respectively. Thus

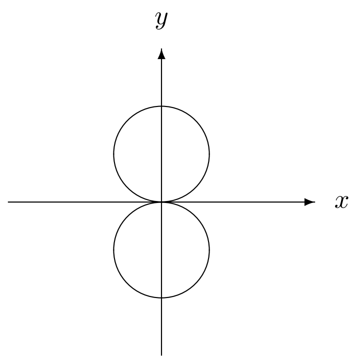
$$\int_0^\infty r^2\,dr\,R_{20}^*(r)\,r\,R_{21}(r) = \frac{a_0}{4\sqrt{3}}\left[(24)-\frac{1}{2}(120)\right] = -\frac{9}{\sqrt{3}}a_0$$

**All together** now:

$$\langle 200|H'|210\rangle = eE\left(-\frac{9}{\sqrt{3}}a_0\right)\left(\frac{1}{\sqrt{3}}\right) = -3eEa_0.$$

**b. Average positions.**
Find $\langle\vec{r}\rangle$ via $\langle x\rangle$, $\langle y\rangle$, $\langle z\rangle$.

State $|2,1,+1\rangle$ has a wavefunction proportional to $Y_1^{+1}(\theta,\phi)$.
State $|2,1,-1\rangle$ has a wavefunction proportional to $Y_1^{-1}(\theta,\phi)$.
So both states have angular distributions as suggested by




From which it's clear that $\langle x\rangle = \langle y\rangle = \langle z\rangle = 0$.

The two remaining states of interest are

$$\begin{aligned}\frac{1}{\sqrt{2}}[|2,0,0\rangle \pm |2,1,0\rangle] &= \frac{1}{\sqrt{2}}[R_{20}(r)Y_0^0(\theta,\phi) \pm R_{21}(r)Y_1^0(\theta,\phi)] \\ &= \frac{1}{\sqrt{2}}\sqrt{\frac{1}{4\pi}}[R_{20}(r) \pm \sqrt{3}\,R_{21}(r)\cos(\theta)].\end{aligned}$$

This is independent of $\phi$, so $\langle x\rangle = \langle y\rangle = 0$. We evaluate $\langle z\rangle$ with the help of the matrix element calculated in part (a):

$$\begin{aligned}\langle z\rangle &= \frac{1}{2}\left[(\langle 2,0,0| \pm \langle 2,1,0|)\, z\, (|2,0,0\rangle \pm |2,1,0\rangle)\right] \\ &= \frac{1}{2}[\underbrace{\langle 2,0,0|z|2,0,0\rangle}_{0} \pm 2\underbrace{\langle 2,0,0|z|2,1,0\rangle}_{-3a_0} + \underbrace{\langle 2,1,0|z|2,1,0\rangle}_{0}] \\ &= \mp 3a_0\end{aligned}$$

Thus, for the latter two states,

$$\langle\vec{r}\rangle = \mp 3a_0\hat{z}.$$

**c.** Escape from contradiction.
If two different *probability densities* both have $\langle z\rangle = 0$, then any combination of those densities has $\langle z\rangle = 0$. But if two *wavefunctions* (or "probability amplitude densities") both have $\langle z\rangle = 0$, then a combination of those wavefunctions might have $\langle z\rangle \neq 0$. What is the **physical principle** behind this mathematical fact? My favorite answer is "Interference", because in interference experiments finite probability (to go

thorough one slit) plus finite probability (to go through another slit) can sum to zero probability (to go through both slits) — thereby showing that the physically controlling entity is not probability density, but something deeper that we eventually found to be wavefunction. But answers of "Superposition" or "The wavefunction has phase as well as amplitude" or "The wavefunction contains more information than the probability density" or "Probability density alone doesn't specify a state" or "Square of sum, not sum of squares" or "Crossterms" are also fine.

**d. Visualize.** I don't have a good answer for this problem.

**e. Find the Hamiltonian matrix.** Stark effect for $n = 3$:
this is a $9 \times 9$ matrix. . . 81 integrals. . . looks pretty formidable!

BUT. . . general rules

$\langle n\ell m|z|n\ell m\rangle = 0$
$\langle n\ell m|z|n'\ell' m'\rangle = 0$ unless $m = m'$
For $\langle n\ell m|z|n'\ell' m\rangle$, the part involving angle $\phi$ is $\int_0^{2\pi} d\phi\, e^{-im\phi} e^{+im\phi} = 2\pi$, so the matrix elements are pure real!

So we arrange the states in the order

$$|300\rangle,\ |310\rangle,\ |320\rangle,\ |311\rangle,\ |321\rangle,\ |31\,{-1}\rangle,\ |32\,{-1}\rangle,\ |322\rangle,\ |32\,{-2}\rangle.$$

The general rules find our non-zero matrix elements:

$$\begin{array}{c}
\begin{array}{ccccccccc} \langle 00| & \langle 10| & \langle 20| & \langle 11| & \langle 21| & \langle 1\bar{1}| & \langle 2\bar{1}| & \langle 22| & \langle 2\bar{2}| \end{array} \\
\left[\begin{array}{ccccccccc}
0 & A & B & & & & & & \\
A & 0 & C & & & & & & \\
B & C & 0 & & & & & & \\
 & & & 0 & D & & & & \\
 & & & D & 0 & & & & \\
 & & & & & 0 & E & & \\
 & & & & & E & 0 & & \\
 & & & & & & & 0 & \\
 & & & & & & & & 0
\end{array}\right]
\end{array}
\begin{array}{c} \\ |00\rangle \\ |10\rangle \\ |20\rangle \\ |11\rangle \\ |21\rangle \\ |1\bar{1}\rangle \\ |2\bar{1}\rangle \\ |22\rangle \\ |2\bar{2}\rangle \end{array}$$

(The kets and bras at the borders of this matrix are $|\ell m\rangle$ or $\langle \ell m|$. . . the value $n = 3$ is not shown because it is the same in all cases. The value $-2$ is shown as $\bar{2}$ because otherwise it messes up the spacing.)

Some of these matrix elements are easy:

$$\begin{aligned}
B &= \langle 20|z|00\rangle \\
&= \int_0^\infty r^2\, dr\, R_{32}(r)\, r\, R_{30}(r) \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi \underbrace{Y_2^{0*}(\theta,\phi)}_{\sim (3\cos^2\theta - 1)} \cos\theta \underbrace{Y_0^0(\theta,\phi)}_{\sim 1}
\end{aligned}$$

$$\begin{aligned}
&\sim \int_0^\pi \sin\theta\, d\theta\, (3\cos^2\theta - 1)\cos\theta \qquad \text{[Then use } \mu = \cos\theta\ldots]\\
&= \int_{-1}^{+1} (3\mu^2 - 1)\mu\, d\mu \qquad \text{[But integrand is odd so...]}\\
&= 0
\end{aligned}$$

[**Moral of the story:** Evaluate the angular integral first. . . it's more likely to vanish.]

Other relationships are also easy to find:

$$\begin{aligned}
D &= \langle 2,1|z|1,1\rangle = \int_0^\infty r^2\, dr\, R_{32}(r)\, r\, R_{31}(r) \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\, Y_2^{1*}(\theta,\phi)\, \cos\theta\, Y_1^1(\theta,\phi)\\
E &= \langle 2,-1|z|1,-1\rangle = \int_0^\infty r^2\, dr\, R_{32}(r)\, r\, R_{31}(r) \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\, Y_2^{-1*}(\theta,\phi)\, \cos\theta\, Y_1^{-1}(\theta,\phi)
\end{aligned}$$

But $Y_2^{-1} = -(Y_2^1)^*$ and $Y_1^{-1} = -(Y_1^1)^*$, so $D = E$.

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[Material below this line uses atomic units, plus the tables on Griffiths pages 139 and 154.]

But some matrix elements are hard:

$$A = \langle 10|z|00\rangle = \underbrace{\int_0^\infty r^2\, dr\, R_{31}(r)\, r\, R_{30}(r)}_{\equiv A_{\text{radial}}} \underbrace{\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\, Y_1^{0*}(\theta,\phi)\, \cos\theta\, Y_0^0(\theta,\phi)}_{\equiv A_{\text{angular}}}$$

$$\begin{aligned}
A_{\text{angular}} &= \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi \left[\sqrt{\frac{3}{4\pi}}\cos\theta\right] \cos\theta \left[\sqrt{\frac{1}{4\pi}}\right]\\
&= \frac{\sqrt{3}}{4\pi}(2\pi) \int_0^\pi \sin\theta\, d\theta\, \cos^2\theta \qquad \text{[Use } \mu = \cos\theta\ldots]\\
&= \frac{\sqrt{3}}{2} \int_{-1}^{+1} \mu^2\, d\mu = \sqrt{3}\int_0^1 \mu^2\, d\mu = \sqrt{3}\left[\tfrac{1}{3}\mu^3\right]_0^1 = \frac{1}{\sqrt{3}}
\end{aligned}$$

$$\begin{aligned}
A_{\text{radial}} &= \int_0^\infty r^2\, dr \left[\frac{8}{27\sqrt{6}}\left(1 - \tfrac{1}{6}r\right) r e^{-r/3}\right] r \left[\frac{2}{\sqrt{27}}\left(1 - \tfrac{2}{3}r + \tfrac{2}{27}r^2\right) e^{-r/3}\right]\\
&= \frac{2^4}{3^5\sqrt{2}} \int_0^\infty dr\, r^4 \left(1 - \tfrac{1}{6}r\right)\left(1 - \tfrac{2}{3}r + \tfrac{2}{27}r^2\right) e^{-2r/3} \qquad \text{[Use } u = \tfrac{2}{3}r\ldots]\\
&= \frac{2^4}{3^5\sqrt{2}} \left(\frac{3}{2}\right)^5 \int_0^\infty du\, u^4 \left(1 - \tfrac{1}{4}u\right)\left(1 - u + \tfrac{1}{6}u^2\right) e^{-u}\\
&= \frac{1}{2\sqrt{2}} \int_0^\infty du\, \left[u^4 - \tfrac{5}{4}u^5 + \tfrac{5}{12}u^6 - \tfrac{1}{24}u^7\right] e^{-u}\\
&= \frac{1}{2\sqrt{2}} \left[4! - \tfrac{5}{4}5! + \tfrac{5}{12}6! - \tfrac{1}{24}7!\right]\\
&= -\frac{18}{\sqrt{2}}
\end{aligned}$$

$$A = \left(-\frac{18}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}}\right) = -3\sqrt{6}$$

$$C = \langle 20|z|10\rangle = \underbrace{\int_0^\infty r^2\,dr\,R_{32}(r)\,r\,R_{31}(r)}_{\equiv C_{\text{radial}}}\underbrace{\int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi\,Y_2^{0*}(\theta,\phi)\,\cos\theta\,Y_1^0(\theta,\phi)}_{\equiv C_{\text{angular}}}$$

$$\begin{aligned}
C_{\text{angular}} &= \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi\,\left[\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)\right]\cos\theta\,\left[\sqrt{\frac{3}{4\pi}}\cos\theta\right] \\
&= \frac{\sqrt{15}}{8\pi}(2\pi)\int_{-1}^{+1}(3\mu^2-1)\mu^2\,d\mu \qquad [\text{Using } \mu=\cos\theta.\ ] \\
&= \frac{\sqrt{15}}{2}\int_0^1 (3\mu^4-\mu^2)\,d\mu \\
&= \frac{\sqrt{15}}{2}\left[\tfrac{3}{5}\mu^5-\tfrac{1}{3}\mu^3\right]_0^1 = \frac{2}{\sqrt{15}}
\end{aligned}$$

$$\begin{aligned}
C_{\text{radial}} &= \int_0^\infty r^2\,dr\,\left[\frac{4}{81\sqrt{30}}r^2e^{-r/3}\right]\,r\,\left[\frac{8}{27\sqrt{6}}\left(1-\tfrac{1}{6}r\right)re^{-r/3}\right] \\
&= \frac{2^4}{3^8\sqrt{5}}\int_0^\infty dr\,r^6\left(1-\tfrac{1}{6}r\right)e^{-2r/3} \qquad [\text{Use } u=\tfrac{2}{3}r\ldots] \\
&= \frac{2^4}{3^8\sqrt{5}}\left(\frac{3}{2}\right)^7\int_0^\infty du\,u^6\left(1-\tfrac{1}{4}u\right)e^{-u} \\
&= \frac{1}{3\cdot 2^3\sqrt{5}}\left[6!-\tfrac{1}{4}7!\right] \\
&= -\frac{9\sqrt{5}}{2}
\end{aligned}$$

$$C = \left(-\frac{9\sqrt{5}}{2}\right)\left(\frac{2}{\sqrt{15}}\right) = -3\sqrt{3}$$

$$D = \langle 21|z|11\rangle = \underbrace{\int_0^\infty r^2\,dr\,R_{32}(r)\,r\,R_{31}(r)}_{\equiv C_{\text{radial}}}\underbrace{\int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi\,Y_2^{1*}(\theta,\phi)\,\cos\theta\,Y_1^1(\theta,\phi)}_{\equiv D_{\text{angular}}}$$

$$\begin{aligned}
D_{\text{angular}} &= \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi\,\left[-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi}\right]\cos\theta\,\left[-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}\right] \\
&= \frac{3\sqrt{5}}{8\pi}(2\pi)\int_0^\pi \sin\theta\,d\theta\,\sin^2\theta\cos^2\theta \qquad [\text{Use } \mu=\cos\theta,\ \sin^2\theta = 1-\mu^2\ldots] \\
&= \frac{3\sqrt{5}}{4}\int_{-1}^{+1}(1-\mu^2)\mu^2\,d\mu \\
&= \frac{3\sqrt{5}}{2}\int_0^1(\mu^2-\mu^4)\,d\mu \\
&= \frac{3\sqrt{5}}{2}\left[\tfrac{1}{3}\mu^3-\tfrac{1}{5}\mu^4\right]_0^1 = \frac{1}{\sqrt{5}}
\end{aligned}$$

Whence, remembering the value of $C_{\text{radial}}$,

$$D = \left(-\frac{9\sqrt{5}}{2}\right)\left(\frac{1}{\sqrt{5}}\right) = -\frac{9}{2}$$

[End use of atomic units.]

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Thus the matrix of the perturbation $\hat{H}'$ is

$$eEa_0 \begin{bmatrix} 0 & -3\sqrt{6} & 0 & & & & & & \\ -3\sqrt{6} & 0 & -3\sqrt{3} & & & & & & \\ 0 & -3\sqrt{3} & 0 & & & & & & \\ & & & 0 & -9/2 & & & & \\ & & & -9/2 & 0 & & & & \\ & & & & & 0 & -9/2 & & \\ & & & & & -9/2 & 0 & & \\ & & & & & & & 0 & \\ & & & & & & & & 0 \end{bmatrix}$$

**f. Diagonalize** this matrix to find the eigenvalues and degeneracies.
Each of the submatrix blocks can be diagonalized independently.

Diagonalize a submatrix of the form $\begin{bmatrix} 0 & D \\ D & 0 \end{bmatrix}$:

$$\det \begin{bmatrix} -\lambda & D \\ D & -\lambda \end{bmatrix} = 0 \quad \Longrightarrow \quad \lambda^2 - D^2 = 0 \quad \Longrightarrow \quad \lambda = \pm D.$$

Or, in our case, $\lambda = \pm eEa_0(9/2)$.

Diagonalize a submatrix of the form $\begin{bmatrix} 0 & A & 0 \\ A & 0 & C \\ 0 & C & 0 \end{bmatrix}$:

$$\begin{aligned} \det \begin{bmatrix} -\lambda & A & 0 \\ A & -\lambda & C \\ 0 & C & -\lambda \end{bmatrix} &= 0 \\ -\lambda \det \begin{bmatrix} -\lambda & C \\ C & -\lambda \end{bmatrix} - A \det \begin{bmatrix} A & C \\ 0 & -\lambda \end{bmatrix} &= 0 \\ -\lambda[\lambda^2 - C^2] - A[-A\lambda] &= 0 \\ \lambda(-\lambda^2 + C^2 + A^2) &= 0 \end{aligned}$$

Resulting in $\lambda = 0, \pm\sqrt{A^2 + C^2}$.
Or, in our case, $\lambda = 0, \pm eEa_0(9)$.

Thus the first-order energy shifts are

$$\begin{array}{cl} +9eEa_0 & \text{(degeneracy 1)} \\ +\frac{9}{2}eEa_0 & \text{(degeneracy 2)} \\ 0 & \text{(degeneracy 3)} \\ -\frac{9}{2}eEa_0 & \text{(degeneracy 2)} \\ -9eEa_0 & \text{(degeneracy 1)} \end{array}$$