

STARK EFFECT IN HYDROGEN FOR N = 3 - HYDROGEN WAVE FUNCTIONS IN MAPLE

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To calculate the Stark effect for $n = 3$ in hydrogen, we *could* work out all the $n = 3$ wave functions and then grind through the integrals required to generate the elements of the matrix W in degenerate perturbation theory. However, this problem presents a good opportunity to see how to handle it with software, using Maple.

First, we need to represent the full, normalized hydrogen wave function, which is given as equation 4.89 in Griffiths:

$$|nlm\rangle = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) \right] Y_l^m(\theta, \phi) \quad (1)$$

where L is an associated Laguerre polynomial and Y is a spherical harmonic.

We can represent this in Maple using the function definition in Fig. 1.

In this definition, *LaguerreL* is Maple's built-in associated Laguerre polynomial. The last bit tells Maple to convert the spherical harmonic *SphericalY* so that it is expressed in terms of Legendre polynomials, as given in equation 4.32 in Griffiths:

$$Y_l^m(\theta, \phi) = (-1)^n \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta) \quad (2)$$

The arguments t and p passed to *SphericalY* are θ and ϕ respectively. This definition is needed to ensure that Maple uses the correct normalization for

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psi(n, l, m) := sqrt(
  ( (2/(n*a))^3 * factorial(n-l-1) ) /
  ( 2*n * (factorial(n+l)) ) ) *
  exp(-r/(n*a)) * (2*r/(n*a))^l *
  simplify( LaguerreL(n-l-1, 2*l+1, 2*r/(n*a)),
  'LaguerreL' ) *
  simplify( convert(SphericalY(l, m, t, p), LegendreP), 'LegendreP' )
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FIGURE 1. Hydrogen wave function in Maple.

the spherical harmonics. This is a handy definition to port over to any problem that requires calculations using the hydrogen wave functions. With this definition, we can now work out the matrix elements of W , which are $W_{ab} = \langle a | eE_{ext}r \cos\theta | b \rangle$ where a and b are chosen from the nine states $|3lm\rangle$, where $l = 0, 1$, or 2 and $m = -l \dots +l$. With the states listed in the order $|nlm\rangle = |300\rangle, |311\rangle, |310\rangle, |31-1\rangle, |322\rangle, |321\rangle, |320\rangle, |32-1\rangle, |32-2\rangle$, the matrix is

$$W = eE_{ext}a \begin{bmatrix} 0 & 0 & -3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{9}{2} & 0 & 0 & 0 \\ -3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & -3\sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{9}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{9}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -3\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{9}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (3)$$

We can use Maple's *LinearAlgebra* package to work out the eigenvalues and eigenvectors. The eigenvalues are 0 (degeneracy 3), $\pm 9eE_{ext}a$ (degeneracy 1 each) and $\pm \frac{9}{2}eE_{ext}a$ (degeneracy 2 each). The corresponding eigenvectors are:

For eigenvalue 0 there are 3 'good' states:

$$\sqrt{\frac{2}{3}} \left(-\frac{\sqrt{2}}{2} |300\rangle + |320\rangle \right), |322\rangle, |32-2\rangle \quad (4)$$

For eigenvalue $-9eE_{ext}a$ there is only 1 state:

$$\frac{1}{\sqrt{6}} \left(\sqrt{2} |300\rangle + \sqrt{3} |310\rangle + |320\rangle \right) \quad (5)$$

For eigenvalue $9eE_{ext}a$ there is one state:

$$\frac{1}{\sqrt{6}} \left(\sqrt{2} |300\rangle - \sqrt{3} |310\rangle + |320\rangle \right) \quad (6)$$

For eigenvalue $-\frac{9}{2}eE_{ext}a$ there are 2 states:

$$\frac{1}{\sqrt{2}} (|311\rangle + |321\rangle), \frac{1}{\sqrt{2}} (|31-1\rangle + |32-1\rangle) \quad (7)$$

For eigenvalue $\frac{9}{2}eE_{ext}a$ there are 2 states:

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$$\frac{1}{\sqrt{2}}(-|311\rangle + |321\rangle), \frac{1}{\sqrt{2}}(-|31-1\rangle + |32-1\rangle) \quad (8)$$