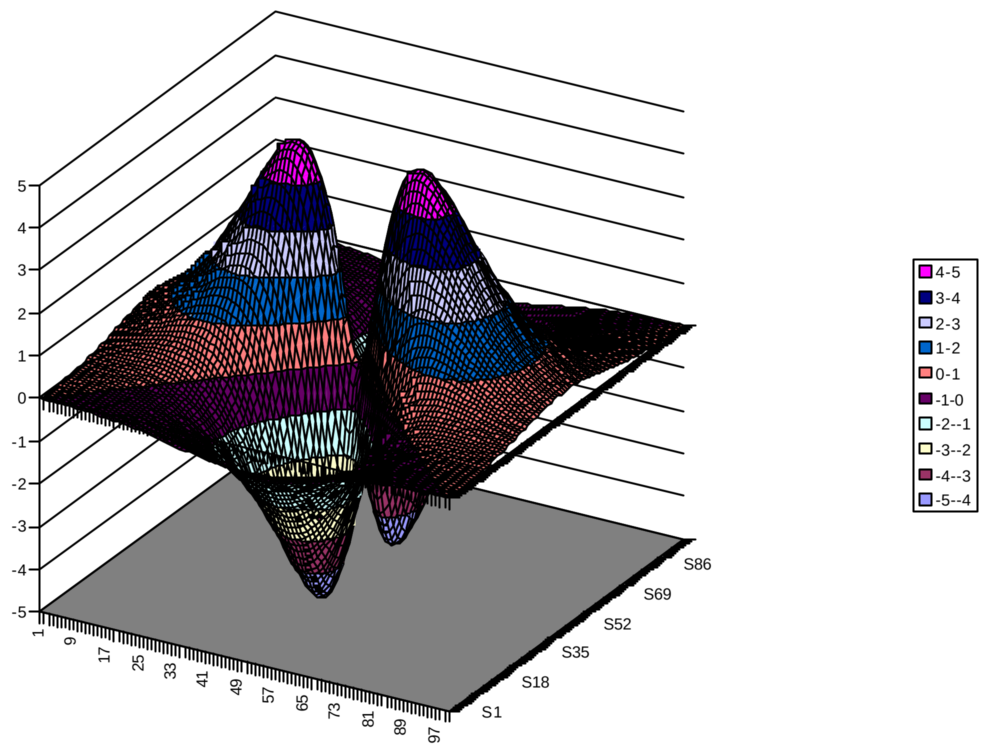
CHEMISTRY 3BB3 1999/2000

Alex Bain

SOLUTIONS TO ASSIGNMENT 2

1. Using a spreadsheet, plot out part of the wavefunction for a $3d_{xy}$ hydrogen atom orbital. The formula for this orbital is proportional to $r^2 e^{-r} \sin^2\theta \cos 2\phi$. Plot this in the *xy* plane, so that $\sin\theta = 1$. Create a 100x100 grid of x and y points, and then use the fact that $r^2 = x^2 + y^2$ and that $\tan\phi = y/x$ (you will find the ATAN2 function useful here). Plot the value of the wavefunction using a surface plot, and then plot the one dimensional cross-sections along the x and y axes.



2. Suppose we use a function of the form Ae^{-cr^2} as a trial wavefunction for the radial part of the H atom.

(a) Evaluate the normalization constant, *A*.

The wavefunction must be normalized, so the integral of the square of the wavefunction must be 1. Remember that in spherical polar coordinates, the volume element is $r^2 dr$ (if we ignore the θ and ϕ parts, which cancel out). The following integrals may be useful.

$$\int_0^\infty r^{2n+1} e^{-ar^2} dr = \frac{n!}{2a^{n+1}}$$

$$\int_0^\infty r^{2n} e^{-ar^2} dr = \frac{1*3*5*...*(2n-1)}{2^{n+1}a^n}\sqrt{\frac{p}{a}}$$

For this case

$$\int_0^\infty e^{-cr^2} \times e^{-cr^2} r^2 dr = \int_0^\infty e^{-2cr^2} r^2 dr$$

$$= \frac{1}{8}\sqrt{\frac{p}{2c^3}}$$

So, the normalization constant, *A*, is given by

$$A^2 = 8\sqrt{\frac{2c^3}{p}}$$

(b) Using the variation principle, calculate the “best” value for the constant c.

The variation integral is given by (remember the factor of r^2 comes from the volume element in polar coordinates).

$$W = \frac{\int \psi^* H \psi \; r^2 dr}{\int \psi^* \psi \; r^2 dr}$$

The Hamiltonian for the radial function is

$$H = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \quad - \quad \frac{e^2}{4\pi\varepsilon_0 r}$$

First we apply the Hamiltonian to the wavefunction

$$\begin{aligned}
H\psi &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} A e^{-cr^2} \quad - \quad \frac{e^2}{4\pi\varepsilon_0 r} A e^{-cr^2} \\
&= A\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}(-2cr^3)e^{-cr^2}\right] - \quad A\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}e^{-cr^2} \\
&= A\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}(-6cr^2 + 4c^2r^4)e^{-cr^2}\right] - \quad A\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}e^{-cr^2} \\
&= A\left[-\frac{\hbar^2}{2m}(-6c + 4c^2r^2)e^{-cr^2}\right] - \quad A\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}e^{-cr^2}
\end{aligned}$$

Then we multiply by ψ and integrate over r. Remember the r^2 in the volume element.

$$\int_0^\infty \psi H \psi \; r^2 dr = A^2 \int_0^\infty e^{-cr^2}\left[-\frac{\hbar^2}{2m}(-6c + 4c^2r^2)e^{-cr^2}\right] r^2 dr - A^2 \int_0^\infty e^{-cr^2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}e^{-cr^2} r^2 dr$$

$$= A^2 \int_0^\infty e^{-cr^2}\left[-\frac{\hbar^2}{2m}(-6c + 4c^2r^2)e^{-cr^2}\right] r^2 dr - A^2 \int_0^\infty e^{-cr^2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}e^{-cr^2} r^2 dr$$

$$= A^2\left[\frac{\hbar^2}{2m}6c\int_0^\infty r^2 e^{-2cr^2}dr - \frac{\hbar^2}{2m}4c^2\int_0^\infty r^4 e^{-2cr^2}dr\right] - A^2\frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r\, e^{-2cr^2}dr$$

Using the integrals above

$$= A^2\left[\frac{\hbar^2}{2m}6c\frac{1}{8}\sqrt{\frac{\pi}{2c^3}} - \frac{\hbar^2}{2m}4c^2\frac{3}{32c^3}\sqrt{\frac{\pi}{2c}}\right] - A^2\frac{e^2}{4\pi\varepsilon_0}\frac{1}{4c}$$

$$= A^2\left[\frac{\hbar^2}{2m}\frac{3}{4}\sqrt{\frac{\pi}{2c}} - \frac{\hbar^2}{2m}\frac{3}{8}\sqrt{\frac{\pi}{2c}}\right] - A^2\frac{e^2}{4\pi\varepsilon_0}\frac{1}{4c}$$

$$= A^2\frac{\hbar^2}{2m}\frac{3}{8}\sqrt{\frac{\pi}{2c}} - A^2\frac{e^2}{4\pi\varepsilon_0}\frac{1}{4c}$$

Since $A^2 = 8\sqrt{\frac{2c^3}{\pi}}$ the variation integral becomes

$$\frac{\hbar^2}{2m}3c - \frac{e^2}{4\pi\varepsilon_0}2\sqrt{\frac{2c}{\pi}}$$

If we take the derivative of this with respect to c, set that to zero, and solve for c, we get

$$\frac{3\hbar^2}{2m} = \frac{e^2}{4\pi\varepsilon_0}\sqrt{\frac{2}{\pi c}}$$

so that

$$c = \frac{8}{9}\frac{e^4 m^2}{(4\pi\varepsilon_0)^2 \pi \hbar^4}$$

and while we are at it

$$\sqrt{\frac{2c}{\pi}} = \frac{4}{3\pi}\frac{e^2}{4\pi\varepsilon_0}\frac{m}{\hbar^2}$$

Substituting this into the value for the variation integral above gives

$$W = -\frac{4}{3\pi}\frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2}$$

$$= -\frac{4}{3\pi} \text{ (in atomic units)}$$

$$= -0.4244$$

(c) Compare the expectation value of the Hamiltonian over this wavefunction with the true energy.

In atomic units, the true energy is -1/2 atomic units. The atomic unit of energy is $\frac{e^2}{4\pi\varepsilon_0 a_0}$,

and the Bohr radius, a_0, is $\frac{4\pi\varepsilon_0\hbar^2}{me^2}$

3. In spherical polar coordinates, the operator that corresponds to the square of the length of the angular momentum vector is

$$L^2 = \left(\frac{-1}{\sin\theta}\right)\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Apply this operator to the (2,0), (2,1) and the (2,2) spherical harmonics (Harris & Bertolucci, page 113), and show that each is an eigenfunction of L^2 with eigenvalue $J(J+1)$, where J is the total angular momentum.

For example, the (2,1) spherical harmonic is $\sin\theta\cos\theta\, e^{i\phi}$. If we apply the operator to this, we get.

$$\left(\frac{-1}{\sin q}\right)\frac{\partial}{\partial q}\left[\sin q\,\frac{\partial}{\partial q}\sin q\,\cos q\;e^{if}\right]-\frac{1}{\sin^2 q}\frac{\partial^2}{\partial f^2}\sin q\,\cos q\;e^{if}$$
$$=\left(\frac{-1}{\sin q}\right)\frac{\partial}{\partial q}\left[\sin q\left(\cos^2 q-\sin^2 q\right)\right]e^{if}-\frac{1}{\sin^2 q}\left(i^2\right)\sin q\,\cos q\;e^{if}$$
$$=\left(\frac{-1}{\sin q}\right)\frac{\partial}{\partial q}\left[\sin q\,\cos 2q\right]e^{if}+\frac{1}{\sin^2 q}\sin q\,\cos q\;e^{if}$$
$$=\left(\frac{-1}{\sin q}\right)\left[\cos q\,\cos 2q-2\sin q\,\sin 2q\right]e^{if}+\frac{1}{\sin^2 q}\sin q\,\cos q\;e^{if}$$
$$=\left(\frac{-1}{\sin q}\right)\left[\cos q(1-2\sin^2 q)-4\sin^2 q\,\cos q\right]e^{if}+\frac{1}{\sin^2 q}\sin q\,\cos q\;e^{if}$$
$$=-\frac{\cos q}{\sin q}e^{if}+6\sin q\,\cos q\,e^{if}+\frac{\cos q}{\sin q}e^{if}$$
$$=2(2+1)\sin q\,\cos q\,e^{if}$$

4. Calculate the eigenvalues of the following matrix

$$\begin{pmatrix} 17 & 13 & -2 \\ 13 & 4 & 7 \\ -2 & 7 & 25 \end{pmatrix}$$

To solve the associated cubic equation, use a solver program (for example, Matlab), or plot the function out using a spreadsheet, and estimate the roots to within +/- 0.05.

The eigenvalues are 23.7407, 27.9023, -5.6430. Note that their sum is the same as 17+4+25. The sum of the diagonal elements of a matrix (the *trace*) is preserved under any unitary transformation.