the computer bulletin board

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Quantum Mechanics Using Mathcad 3.0

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MathSoft has recently released a Windows version of Mathcad. The live document feature of Mathcad 3.0 (*1*) running under the graphical interface of Windows 3.0 (*2*) provides a powerful computational and programming environment for a wide variety of calculations encountered in the traditional physical chemistry sequence.

This note describes three quantum mechanical calculations appropriate for an undergraduate course: numerical solutions for Schrödinger's equation, the linear variation method, and molecular orbital theory. Applications of earlier releases of Mathcad in physical chemistry have been described by others (*1*, *2*).

Numerical Solutions for Schrödinger's Equation

The use of basic programs and spreadsheet templates to obtain numerical solutions for Schrödinger's equation has previously been described (*3–5*). Mathcad offers a significant pedagogical advantage over either of these alternatives. Figure 1 shows a Mathcad document for finding numerical solutions for the radial part of Schrödinger's equation.

Text, mathematics, and graphics are integrated into one live document on the screen just as they would customarily appear in a textbook, on a blackboard, or in a set of lecture notes. With appropriate scaling of the graphical display, the screen can simultaneously present the following.

- the parameters
- the integration algorithm (*6*)
- a graphical display of the solution

To find solutions for the hydrogen atom, for example, the user sets the values for the integration grid, integration limits, electron mass, nuclear charge, and angular momentum, and then makes a guess for the energy eigenvalue. In the automatic recalculation mode, all equations are recalculated, and the screen is refreshed with current graphics.

If the wavefunction satisfies the right-hand boundary condition, a solution has been found. If not, another guess for the energy is made. In general, it is not difficult to bracket the correct energy eigenvalue and move quickly to a solution. On a 80486 25-MHz machine with an integration grid of 300, the screen was refreshed in two seconds.

By editing the potential energy term one can use the same document to solve a variety of problems, such as

- particle in the infinite spherical potential well
- three-dimensional isotropic oscillator

All the traditional one-dimensional problems can be solved with a separate document using an algorithm appropriate for the one-dimensional Schrödinger equation (*5*, *7*).

- particle in the box
- simple harmonic oscillator
- Morse potential
- particle on a ring

Thus, by providing students with two Mathcad files of modest size (approximately 5 Kbytes) one can ask them to obtain numerical solutions for all the quantum mechanical problems that are covered in the traditional physical chemistry textbooks—and many that are not.

Integration grid, integration limits, and initial values for the wavefunction:

$n := 300 \quad Rmin := 0 \quad Rmax := 35 \quad \Delta := \frac{Rmax - Rmin}{n} \quad R_0 := 1 \quad R_1 := .99$

Reduced mass: $\mu := 1$ Angular Momentum: $l := 1$ Nuclear charge: $z := 1$

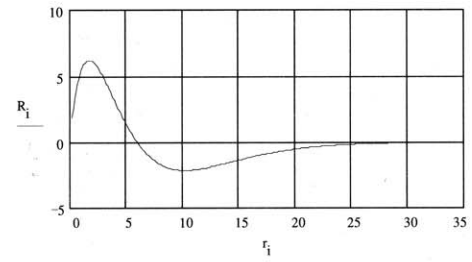
$r_1 := Rmin + \Delta \quad \text{if}(l > 0, R_0 := 0)$

$i := 2, 3 .. n \quad r_i := Rmin + i \cdot \Delta \quad V_{i-1} := \frac{-z}{r_{i-1}}$

$$R_i := \frac{\left[2 \cdot R_{i-1} + \left[l \cdot \frac{(l+1)}{(r_{i-1})^2} - 2 \cdot \mu \cdot (E - V_{i-1})\right] \cdot R_{i-1} \cdot \Delta^2 - \left(1 - \frac{\Delta}{r_{i-1}}\right) \cdot R_{i-2}\right]}{\left(1 + \frac{\Delta}{r_{i-1}}\right)}$$

Enter energy guess: $E = -.055556$

Plot radial wavefunction:



Plot radial distribution function:

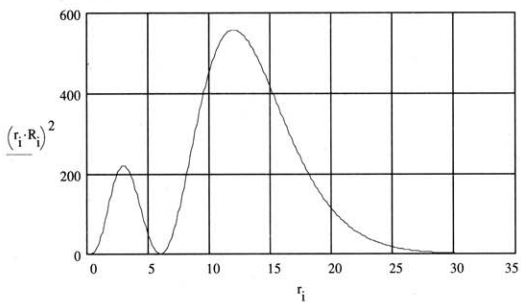


Figure 1. Mathcad document for the numerical integration of the radial equation for the hydrogen atom.

Number of terms in trial wavefunction: $n := 3$ ORIGIN := 1

1. Calculation of matrix elements: $i := 1..n$ $j := 1..n$

$$H_{i,j} := \int_0^1 \sqrt{2}\cdot\sin(i\cdot\pi\cdot x)\cdot\frac{-1}{2}\cdot\frac{d}{dx}\frac{d}{dx}\sqrt{2}\cdot\sin(j\cdot\pi\cdot x)\,dx \ldots + \int_0^1 \sqrt{2}\cdot\sin(i\cdot\pi\cdot x)\cdot 10\cdot x\cdot\sqrt{2}\cdot\sin(j\cdot\pi\cdot x)\,dx$$

2. Display variational matrix and find eigenvalues:

$$H = \begin{pmatrix} 9.935 & -1.801 & 0 \\ -1.801 & 24.739 & -1.945 \\ 0 & -1.945 & 49.412 \end{pmatrix} \qquad \text{eigenvals}(H) = \begin{pmatrix} 9.717 \\ 49.565 \\ 24.804 \end{pmatrix}$$

3. Find eigenvectors:

$a := \text{eigenvec}(H, 9.717)$ $b := \text{eigenvec}(H, 24.804)$ $c := \text{eigenvec}(H, 49.565)$

$$a = \begin{pmatrix} 0.993 \\ 0.12 \\ 0.006 \end{pmatrix} \qquad b = \begin{pmatrix} 0.12 \\ -0.99 \\ -0.078 \end{pmatrix} \qquad c = \begin{pmatrix} -0.004 \\ 0.078 \\ -0.997 \end{pmatrix}$$

4. Plot wavefunction and wavefunction squared for ground-state.

$x := 0, .02 .. 1$

$$\Psi(x) := \frac{\sum_i a_i\cdot\sqrt{2}\cdot\sin(i\cdot\pi\cdot x)}{\sqrt{\sum_i (a_i)^2}}$$

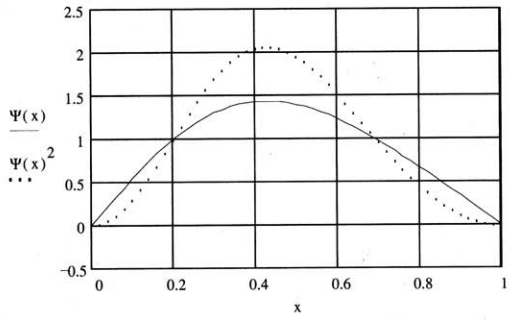


Figure 2. Mathcad document for the variational treatment of the particle in the one-dimensional slanted box, with $V = 10x$.

The Linear Variation Method

Figure 2 shows a Mathcad document that uses the variation method to find approximate solutions to Schrödinger's equation for the particle in the slanted one-dimensional box with potential energy $V = 10x$. In this variational calculation the trial wavefunction is a sum of the first three eigenfunctions for the particle in the one-dimensional box. More terms can be included in the trial function by increasing the value of n.

The matrix elements H_{ij} are calculated in section 1. The eigenvalues and eigenvectors are calculated in sections 2 and 3 using Mathcad's built-in functions "eigenvals" and "eigenvec". In section 4 the wavefunction and its square are displayed for the ground-state energy. Just as in the previous example, this document can serve as a template for doing a variety of variational calculations. In addition, this exercise can be related to the previous one by asking the students to obtain numerical solutions for the particle in the slanted box and then compare them to the results of the variation method.

Molecular Orbital Theory

Molecular orbital theory is generally introduced with a calculation on the one-electron hydrogen molecule ion (*8*). Figure 3 shows a Mathcad document for a calculation using a linear combination of hydrogen atom 1s orbitals as the molecular orbital. In this calculation the energy is a function of the internuclear separation R.

In section 1, R and the energy are given seed values for the numerical solution algorithm. In section 3, R and the energy are determined using the built-in "Find" function given the constraints expressed in section 2. The constraints are the equation of the energy as a function or R and the first derivative of the energy with respect to R set equal to zero. Finally, in section 4 the bonding molecular orbital is displayed as a surface plot. It is not difficult to revise this document for a molecular orbital calculation using scaled hydrogen 1s orbitals (*9*).

These three examples illustrate the ease of use and the versatility of Mathcad 3.0. The author has also used it in a variety of other applications.

- routine problem solving, including units management
- linear, nonlinear, and polynomial regression analysis
- obtaining roots of transcendental equations
- solving systems of linear equations
- a simple SCF calculation
- NMR simulation

Conclusion

In summary, Mathcad 3.0 running under the graphical user interface of Windows 3.0 provides a pleasant and effective computational environment for doing a variety of traditional quantum mechanical calculations. Its features