
Enriching Quantum Chemistry with Mathcad

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Abstract

Mathcad is a comprehensive, inexpensive program for doing numeric and symbolic mathematics on a computer. Mathcad handles data, text, mathematics, and graphics in a single live document and has an appealing, user-friendly graphical interface. Mathcad has a wide variety of applications in the undergraduate chemistry curriculum, but is especially useful in the mathematically intensive courses traditionally found in the physical chemistry sequence (1, 2, 3, 4). As the title suggests, *Enriching Quantum Chemistry with Mathcad (for Macintosh)* presents applications of Mathcad in the area of quantum chemistry selected from those previously published for Windows (5, 6).

Students generally find quantum chemistry to be highly mathematical, quite difficult, and very abstract. They are right on all counts. However the subject is also extremely important today, even at the undergraduate level. There is, therefore, a need for relatively simple computer exercises that bridge the gap between the formalism of quantum theory and its various computational methods (7). All of the Mathcad documents presented here attempt to do this in one way or another. Some exercises involve relatively elementary problem solving, while others, for example, illustrate the basics of molecular orbital theory and the variational method.

Enriching Quantum Chemistry with Mathcad (for Macintosh) includes Mathcad documents in the following areas:

- Routine problem solving and units management
- Linear, nonlinear, and polynomial regression analysis
- Numerical solutions for Schrödinger's equation
- The variational method
- Hückel Molecular Orbital Theory
- Semi-Empirical MO Calculation on Hydrogen Fluoride
- A Really Simple SCF Calculation
- Spectroscopic Transitions for an Electron in a 1-D Box
- Finding Roots

Getting Started



To start Enriching Quantum Chemistry with Mathcad, first start Mathcad or Mathcad PLUS by double-clicking its icon in the Finder. Select **Open...** from the File menu and navigate to the worksheet you wish to use.

or, you can double-click the icon for the worksheet you want to use. Mathcad will open and the file you selected will be loaded.

Mathcad help is available from the Help menu (System 8) or ? on the right side of the menu bar (System 7). You can quit Mathcad at any time by typing Command-Q. An introduction to Mathcad files in this collection is included. Its file name is INTRO.MCD.

User Directions

The goal of Enriching Quantum Chemistry with Mathcad is to illustrate interesting applications, not to teach Mathcad per se. If you do not have a copy of the Mathcad Users Manual and are unfamiliar with the program, consult your instructor. Each worksheet includes a text introduction to help you get started.

The following is a summary of the applications treated in this software package.

Routine Problem Solving and Units Management

This section consists of a worksheet for doing quantum chemistry problems. In addition to definitions of the commonly used fundamental constants and frequently used conversion factors, it includes several examples of elementary problem solving in quantum chemistry.

Mathcad worksheet: ROUTINE.MCD

Applications of Integral and Differential Calculus in Quantum Mechanics

This section illustrates both numeric and symbolic Mathcad solutions to commonly encountered quantum mechanical problems that directly involve integral and differential calculus.

Mathcad worksheet: CALCULUS.MCD

Regression Analysis

This module illustrates how Mathcad can be used to carry out linear, nonlinear, and polynomial regression analyses for problems that arise in quantum chemistry.

Mathcad worksheets: REGRESS.MCD, PHOTO.MCD, PLANCK.MCD, EINSTEIN.MCD, DEBYE.MCD, FITPOLY.MCD

Numerical Solutions for Schrödinger's Equation

This is probably the most powerful application of Mathcad to quantum mechanical problems. This section illustrates numerical solutions for one-, two-, and three-dimensional problems. The Mathcad documents provided for each of these problems can serve as templates for a large number of quantum mechanical problems.

Mathcad worksheets: NUMSOL.MCD, 1DBOX.MCD, FINITE.MCD, TUNNEL.MCD, MORSE.MCD

Reference

For derivation of integration algorithm see: Bolemon, J. S. *Am. J. Phys.* **1972**, *40*, 1511.

Ab Initio Molecular Orbital Calculation on the Hydrogen Molecule Ion

A simple molecular orbital calculation on H_2^+ based on the LCAO-MO approximation is illustrated, including surface and contour plots.

Mathcad worksheet: MOT60.MCD

Reference

For a simple MO calculation in Fortran see: Robiette, A. G. *J. Chem. Educ.* **1975**, *52*, 95.

Semi-empirical Molecular Orbital Calculations on HF and XeF₂

These calculations are based on Example 14.11 and Problem 14.8 from Atkins' physical chemistry textbook. Several calculational methodologies are presented. The main difference between these calculations and the Huckel calculation that follow is that most of the matrix elements in this calculation are given explicit values based on empirical quantities. This calculation can be extended to hydrogen chloride by using the information provided by Atkins in Exercise 14.11 on page 493.

Mathcad worksheets: HFMOT60.MCD, XEF2.MCD

Reference

Atkins, P. W. *Physical Chemistry*, 5th ed.; W. H. Freeman: New York, 1994; Chapter 14, pp 488-493.

Huckel Molecular Orbital Theory

In this set of Mathcad worksheets, Huckel molecular orbital calculations are done on three molecules; butadiene, benzene, and buckminsterfullerene. These calculations might be described as a strictly numeric Huckel approach because the Huckel matrices are not simplified prior to calculation by the application of symmetry arguments. The Mathcad documents presented in this section can serve as templates for Huckel theory calculations on other molecular systems.

Mathcad Worksheets: HUKINTRO.MCD, BUTADIEN.MCD, BENZENE.MCD, C60.MCD.

Reference

Atkins, P. W. *Physical Chemistry*, 5th ed.; W. H. Freeman: New York, 1994; Chapter 14, pp 496-501.

The Linear Variation Method

The variational method is applied to the particle in the slanted box, the simple harmonic oscillator, the Stark effect, and to the calculation of the nmr spectrum of an ABC nuclear spin system. The Stark effect calculation is actually an example of first order perturbation theory, but is included here as another method of finding approximate solutions to Schrödinger's equation.

Mathcad worksheets: VARMETH.MCD, SLANT.MCD, VARISHO.MCD, STARK.MCD, NMR.MCD

References

Atkins, P. W. *Physical Chemistry*, 5th ed.; W. H. Freeman: New York, 1994; Chapter 14, pp 488-493.

Rae, A. I. *Quantum Mechanics*, 3rd ed.; IOP Publishing Ltd.; Bristol, 1992; pp 147-148.

Johnson, C. S.; Pedersen, L. G. *Problems and Solutions in Quantum Chemistry and Physics*, Dover Publications: New York, 1986.

A Really Simple SCF Calculation

In order to fully appreciate the complexity of molecular SCF calculations carried out by programs like Spartan, HyperChem, Gaussian 92, etc. it is helpful to examine a simple two-electron calculation on the helium atom. The calculation presented here is simple not only because it treats only two electrons, but also because it employs the simplest possible basis set for an atomic calculation. Because of these simplifications the basic elements of the SCF procedure stand out. Three different methods of calculation are presented for this calculation, which is easily extended to other two-electron species.

Mathcad worksheet: HELIMSCF.MCD

Reference

Rioux, F. *Eur. J. Phys.* **1987**, *8*, 297.

Spectroscopic Transitions for an Electron in a One-Dimensional Box

This exercise looks at the fluctuating dipole mechanism for “quantum jumps” as described by McMillin (see reference cited below). The proposed mechanism is used to model transitions for the electron in a one-dimensional box. Mathcad handles complex number arithmetic in a facile manner making it an ideal programming environment for this calculation.

Mathcad worksheet: JUMP.MCD

Reference

McMillin, D. R. *J. Chem. Educ.* **1978**, *55*, 7. Also see: Henderson, G. *J. Chem. Educ.* **1979**, *56*, 631.

Finding Roots

The attempt to find analytical solutions for Schrödinger’s equation frequently yields transcendental equations that can be solved by a combination of graphical and numerical techniques. This exercise shows how Mathcad can be used to find the energy eigenvalues for the particle in a box with an internal barrier. It then compares this solution with a numerical solution for Schrödinger’s equation of the type presented above. (See Numerical Solutions for Schrödinger’s Equation.) This problem could also be successfully treated using the variational method. Thus, it is possible to bring three different computational techniques to bear on the same problem.

Mathcad worksheet: ROOTS.MCD

Reference

Johnson, E. A.; Williams, H. T. *Amer. J. Phys.* **1982**, *50*, 239.

Instructor Notes

The purpose of this software package is to illustrate applications of Mathcad in the field of quantum chemistry. Mathcad has been used successfully for the past six years as a “math toolbox” in a junior-senior level quantum chemistry course at Saint John’s University and the College of Saint Benedict.

By allowing text, data, mathematics, and graphics to be combined into a single live document, Mathcad lends itself well to a wide variety of applications. One obvious application is the preparation of laboratory reports. Its graphical interface presents a pleasant and powerful environment. You can use Mathcad for routine problem solving and units management or you can explore the use of integral and differential calculus in quantum chemistry. More advanced applications include regression analysis, numerical integration of Schrödinger’s equation, ab initio and semi-empirical molecular orbital calculations, Huckel mo-

molecular orbital calculations, the variation method, calculation of the NMR spectra of simple nuclear spin systems, and self-consistent field calculations on two-electron atomic and molecular systems.



The goal here is to illustrate interesting applications, not to teach Mathcad per se. So it is assumed that you possess the Mathcad user's manual and are reasonably familiar with it.

Mathcad documents are easy to edit. This makes it possible for you to modify the existing documents in order to explore alternative conditions. In addition, most of the Mathcad documents presented here can be used as templates that can be easily modified to do different but similar problems. You are encouraged to modify, copy, cut, and paste as you see fit.

These Mathcad documents have been prepared using the Hewlett Packard LaserJet III as the default printer. If your default printer is different you may observe page breaks in peculiar places, such as in the middle of a graph or a matrix. Therefore, you may find it necessary to force a page break or move or resize things. This is very easy to do in Mathcad and, therefore, should not be a source of frustration.

For purposes of uniformity and consistency with the Windows version, 10 point Arial has been chosen as the default font for text, variables, and constants. If you do not have Arial, the text will appear as Helvetica. The font can be easily modified to suit your individual tastes. In addition, the default color for text is blue and for equations it is black. The contrast is helpful and pleasing to the eye. However, these parameters are easily changed to suit your preferences. Refer to the Mathcad user's manual for directions.

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Citations

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