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Book review

Charles M Quinn: Computational Quantum Chemistry: A guide to interactive basis set theory

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This text covers the complexity of basis set theory in great detail. The theme of the text is that of using computational tools provided on the accompanying CD-ROM to illustrate both the broad and the subtle aspects of how basis set parameters affect the results and accuracy of electronic structure calculations. Most of the calculations pertinent to the text are performed using Excel spreadsheets provided on the CD-ROM distributed with the book. These spreadsheets use optimization functionality built into Excel and numeric integration methods programmed by hand. The reader of the text is often referred back to the CD to fiddle with various parameters in the calculations and observe the effect on the output. This output is both numerical and graphical, which is especially useful when comparing different orbital representations by plotting, for example, the radial distribution functions. There is also a Herman–Skillman atomic electronic structure program that runs in DOS mode to compute radial wave functions for many electron atoms, allowing comparison with the linear combination of atomic orbitals–molecular orbital wave functions computed in the spreadsheet.

The first three chapters (114 pages) focus on the essential association between an atomic orbital, as an exact solution to the Schrödinger equation for the hydrogen atom, and a basis function, intended to represent the "location" of an electron in a many-particle system. The author describes several types of analytic functions that have historically been used as localized basis functions in electronic structure calculations, and demonstrates how the various kinetic and potential energy integrals needed for the evaluation of any one-electron property can be obtained. Specific chapter sections address general wave function issues, numerical integration over spatial coordinates, overlap, normalization, and orthonormality for contracted and uncontracted atomic orbital basis sets. Numerous exercises are provided to guide the reader through the rapid generation of a large number of illustrative comparisons between exact and approximate representations of hydrogenic orbitals.

Chapters 4–6 (also 114 pages) apply the techniques from the first half of the text to the calculation of the total electronic energy of some simple atomic and molecular systems. As the author moves to many-electron systems, he briskly reviews the calculation of two-electron integrals over s-type Gaussian basis functions. Because of limitations in the math libraries in many spreadsheet programs, these are the only two-electron integrals presented, limiting the discussion of molecular electronic structure to molecules involving H and He. This, fortunately, focuses the latter half of this book on how a Hartree–Fock self-consistent-field (SCF) calculation proceeds rather than on the reduction of integral equations. The iteration through the SCF procedure is accomplished through a repetitive cut-and-paste process, but does allow the user to become intimately familiar with the feedback cycle characteristic of most SCF and density functional programs. A series of examples demonstrate the calculation of electronic excited states for He, and several bond length and bond dissociation energy calculations for simple diatomics, by pointwise constructing potential-energy curves. Near the end of the final chapter, with some early molecular results in hand, there is a very brief mention of how bonding and antibonding orbitals can be conceptualized through examination of the numerical molecular orbital coefficient matrix. The final paragraphs invite the reader to take the next logical step and continue their investigation of electronic structure calculations through the use of commercial software.

Overall, *Computational Quantum Chemistry: An Interactive Guide to Basis Set Theory* brings together a useful collection of example calculations that take the reader through the early days of computational molecular orbital theory using spreadsheet software to per-

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form the math. I imagine this roughly parallels the work of early theoreticians while avoiding the tedium of paper-and-pencil analysis. This is a substantially mathematical treatment, and the majority of the text is dedicated to precise derivation of relationships and the translation of those relationships into spreadsheet formulae. Because of this, and the way the contents of each spreadsheet build on those previous, the text must generally be followed from beginning to end. Fortunately, it is quite readable, although a surfeit of commas may become a little tedious for some. More than just an exposition of basis set theory, this book serves as a good introduction to the workings of electronic structure code but assumes very little programming experience on the part of the reader. The 85 references are a decent shopping list for anyone wishing to begin a library of the fundamental publications documenting the development of electronic structure theory.