CHIMIA 51 (1997) Nr. 3 (März)

COMPUTATIONAL CHEMISTRY COLUMN

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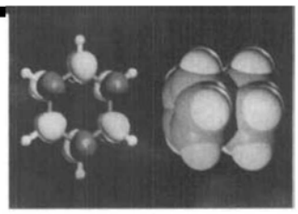

Chimia 51 (1997) 100–106

ISSN 0009–4293

Teaching *ab initio* Quantum Chemistry in a Networked Environment

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Abstract. The World Wide Web (WWW, Web) has blossomed as an information distribution media in both the public and private sectors; the electronic-information technologies are also revolutionizing educational-program development and dissemination. This work presents the practical exercises for an *ab initio* quantum-chemistry course that gives an introduction to the methods of numerical quantum chemistry with the goal of enabling students to perform their own *ab initio* studies. The exercises, which cover a broad range of topics from different areas of physical chemistry, have been developed within the hypertext domain to take advantage of many features unique to this media which are beneficial for instruction purposes. They can be browsed on the World Wide Web at `http://www.scsc.ethz.ch/chem/qcii.html`.

1. The Quantum-Chemistry Course

Over the past ten years, graduate and undergraduate chemistry programs at most universities have started to offer classes in computational chemistry, and teaching has become an increasingly important issue. The demand for textbooks and practical exercises at different levels of skill and background has risen substantially, as has the demand for more effective teaching tools including both hardware and software (see, *e.g.*, the recent article 'Teaching Computational Chemistry Using Computers' by *Weber* and *Morgantini* in the March 1995 issue of this journal [1]).

'Quantenchemie II', taught by *H.P. Lüthi* and *T.-K. Ha* at the Department of Chemistry of the ETH-Zürich, covers the application of theoretical methods available to modern quantum chemistry. The course follows roughly the textbook of *Szabo* and *Ostlund* [2] and consists of 14 class lessons and 7 practical assignments of two class periods each. The practical assignments are not very tightly coupled to the lecture (*i.e.*, no direct contextual link to the lecture material), but rather follow an agenda ensuring that the students acquire the technical skills and the practical understanding to independently perform *ab initio* quantum chemical studies.

The practical assignments do not aim at a steady increase of the complexity of the quantum chemical methodology used, but rather try to address a broad range of chemical phenomena by computation. Therefore, the level of theory used rarely exceeds *Hartree-Fock* (HF), Density-Functional Theory (DFT), and second-order *Møller-Plesset* perturbation theory (MP2). This, of course, also reflects the time limits imposed on the class (90 min per unit; no homework assignments). Therefore, after addressing technical issues such as setting up, submitting, and analyzing computations, the interest shifts towards problems which cover a variety of chemical phenomena from different areas of physical chemistry.

Every lesson is completely self-contained and modular to allow flexibility for adding or modifying lessons to reflect changes in the field. Currently, the modules available focus upon spectroscopic, thermochemical, and structure-energy problems. The *Table* gives an overview over the topics addressed and a brief synopsis of each lesson appears in *Sect. 5*. More complete descriptions of their content and the strategy behind their design can be found in other publications [3][4].

2. Education and the Electronic Media

Education in computational chemistry is in the process of incorporating new tools for effective teaching. Thus, far efforts have focused primarily on mixed-media presentation of graphical examples in lectures and use of the most appropriate software in the lab. When well managed, such as in the courses at the University of Geneva, this can lead to quite effective results [1]. In the field of physics, recent efforts have started taking advantage of hypertext capabilities of WWW browsers to create a unified multimedia lecture environment which even includes some (albeit virtual) lab experiments [5].

On the WWW, the first quantum-chemistry textbooks, such as 'Quantum Chemistry in Molecular Modeling' by *Brouwer* [6], and lecture notes, like 'Fundamental Theory Notes' by *Schaefer*'s research group [7] and 'Theory of Atoms in Molecules' by *Bader* [8], have appeared. Here, though, the Internet and Web are appearing primarily as a means of distribution of an otherwise 'paper' product and the articles do not take advantage of the multiple features unique to the WWW.

With respect to practical assignments for *ab initio* quantum-chemistry classes

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offered on the WWW, there are the North Carolina Supercomputing Center (NCSC) course 'Computational Chemistry for the Undergraduate Curricula' and the 'Australian Computational Chemistry via the Internet Project (ACCVIP)'. The NCSC server addresses the *instructors* of chemistry classes and is available only to faculty, staff, and students of North Carolina [9]. The ACCVIP teaching modules, which are planned to cover a broad range of topics, will only be accessible to the Australian universities participating in the project [10]. Initiatives such as Australia's ACCVIP [10] and ETH-Zürich's 'Network for Educational Technology (NET)' [11] should foster the development and hopefully the exchange of educational materials.

Inspired by the wealth of opportunities newly available *via* electronic media, we decided to present the practical assignments as hypertext markup language (HTML) documents on the WWW (*Fig. 1*). During class, instead of collecting handouts, the students will access the assignments using an HTML browser such as Netscape Navigator [12] or HotJava [13]. The obvious advantages of this approach is that it allows not only for posing the questions on the same monitor where the students work, but also for providing data (basis sets, geometries, *etc.*) in an electronic format which is easy to use. Another bonus of the HTML approach is the possibility to establish hyperlinks to a variety of electronic sources of information (theory, chemical reference data, literature references, *etc.*).

More importantly, however, the WWW is a globally accessible information system. These practical lessons are thus available to teachers and students anywhere in the world. We expect that other educators with focused experience in (the teaching of) a particular area will use this novel medium and that the wealth of assignment modules which become available will be easily linked to expand the current assignment list. Already for Exercise 9, *Thermodynamics and Kinetics* (*vide infra Sect. 5.9*) concerning the equilibrium constant and the rate of reaction for $CH_3 + H_2 \rightarrow CH_4 + H$, the assignment module is linked directly from another Web site [14].

Table. *Topics Addressed in the Practical Assignments*

Assignment	1	2	3	4	5	6	7	8	9	10	11
Chemistry											
Thermodynamics		○	●	●	●	●		●			
IR/Raman		○	●	○	○		○	○	○		
Microwave							●				
Kinetics									●		
NMR										●	
UV/VIS											●
Methodology											
Hartree-Fock Theory		●	●	●	●	○	○	○	○		
Density-Functional Theory		○				●	○	○	○		
2nd-Order Pertubation Theory		○				●	○	○	●		
Higher-Level Correlation						●	○				
Basis-Set Truncation		●	●	●			○	○			
Accuracy *vs.* Comp. Cost		●	○	○		○	●	●			
Technical Aspects											
Molecular Orbital Analysis		●			●						
Stationary Pt. Characterization			●	●	●				●		
Basis Set Superposition Error				●		●					
Size Consistency/Extensivity						●					
Quantitative Accuracy						●	●	○			
Additional Aspects	*a*	*b*			*c*	*d*	*e*		*f*	*g*	*g*

● = topic/skill is required/emphasized; ○ = topic/skill is optional/not stressed; *a* = molecular editor, file handling, HTML browser; *b* = vertical IP *vs. Koppman*'s IP; *c* = *Woodward-Hoffmann* rules; *d* = 2- and 3-body binding energy contributions; *e* = anharmonics; *f* = reaction path following; *g* = planned.

3. Software and Hardware Requirements

The quantum-chemistry software used for the course needs to fulfill several basic requirements. So that the beginning student will have few difficulties, it must be easy to use, having a graphical user interface (GUI) with a molecular editor to ensure efficiency and progress in the class. It should easily allow processing of the input and output data, both graphically and by direct editing of the files. The input generator should provide reasonable defaults, so the student is able to perform simple calculations quickly without *a priori* understanding of *all* the options that the application programs provide. The program should be flexible enough to calculate a variety of levels of theory (or interface with other programs which do). If the quantum chemical application software is not available on the workstation where the user interface is running, the interface should be able to submit and monitor a batch queue job an appropriate system.

For the course, we chose to use the UniChem [15] software system. UniChem is not the only software package offering all the necessary features, and the practical assignments presented here are completely generic and not UniChem-specific. The students ran UniChem on Silicon Graphics Indy workstations in the Department of Chemistry's student laboratory connected to a Cray J90 compute server over the ETH-Zürich campus network. The students worked in teams of two at each workstation with one teaching assistant supervising about three teams. This seemed a very effective balance for an instructor-student ratio and effective use of lab time.

4. Web-Based Execution

In our course, the students used the Netscape [12] HTML browser. This is for three reasons: it is a graphical user interface (GUI) which is easy to use; it is available at no cost to academic institutions, and it supports Java [16] and JavaScript [17] applets. Using applets, small data-processing programs can appear di-

rectly within the 'handouts'. Therefore, it is possible not only to present static text and images, but also to let the students interact with the Web page. Using the browser, they can process output data and visualize the results.

There exist various ways for enabling Web-based execution, two of which have been used for this course. The data-processing programs of the practical exercises, like most computational tasks, consist of three parts: the definition of the input parameters, the actual computation, and the presentation of the output. The two setups we have implemented are:

1. Using *Java applets* executed within the browser for all three parts, *i.e.*, for accepting input data, for doing the computation, and for presenting the output both in numerical and in graphical forms (*vide infra Sect. 4.1*).
2. Using Java applets executed within the browser for the input and for the display of the results, but using *CGI binaries* for the execution of the computation on a remote compute server (*vide infra Sect. 4.2*).

A third possibility which is widespread but which we have not implemented is the use of HTML forms (*i.e.*, form widgets which are part of the HTML definition) for creating the user input interface. Numerous examples of Web-based execution

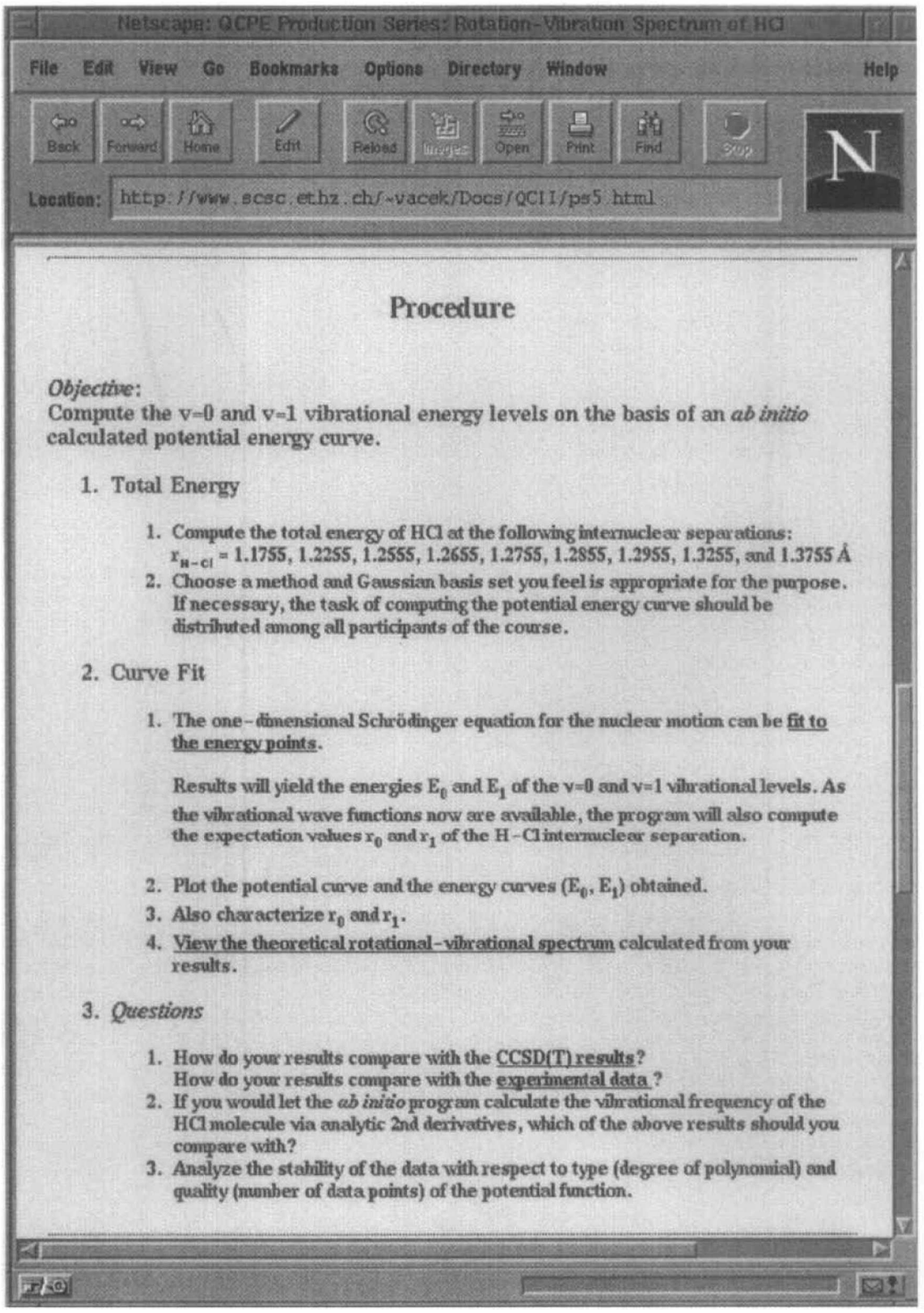

Fig. 1. *Exercise 7*, The Rotation-Vibration Spectrum of HCl, *as seen through the Netscape browser*. Links to other documents appear underlined. For instance, selecting the 'View ...' link will open the document shown in *Fig. 4*. The assignment is preceded by introductory information (note position of scrollbar).

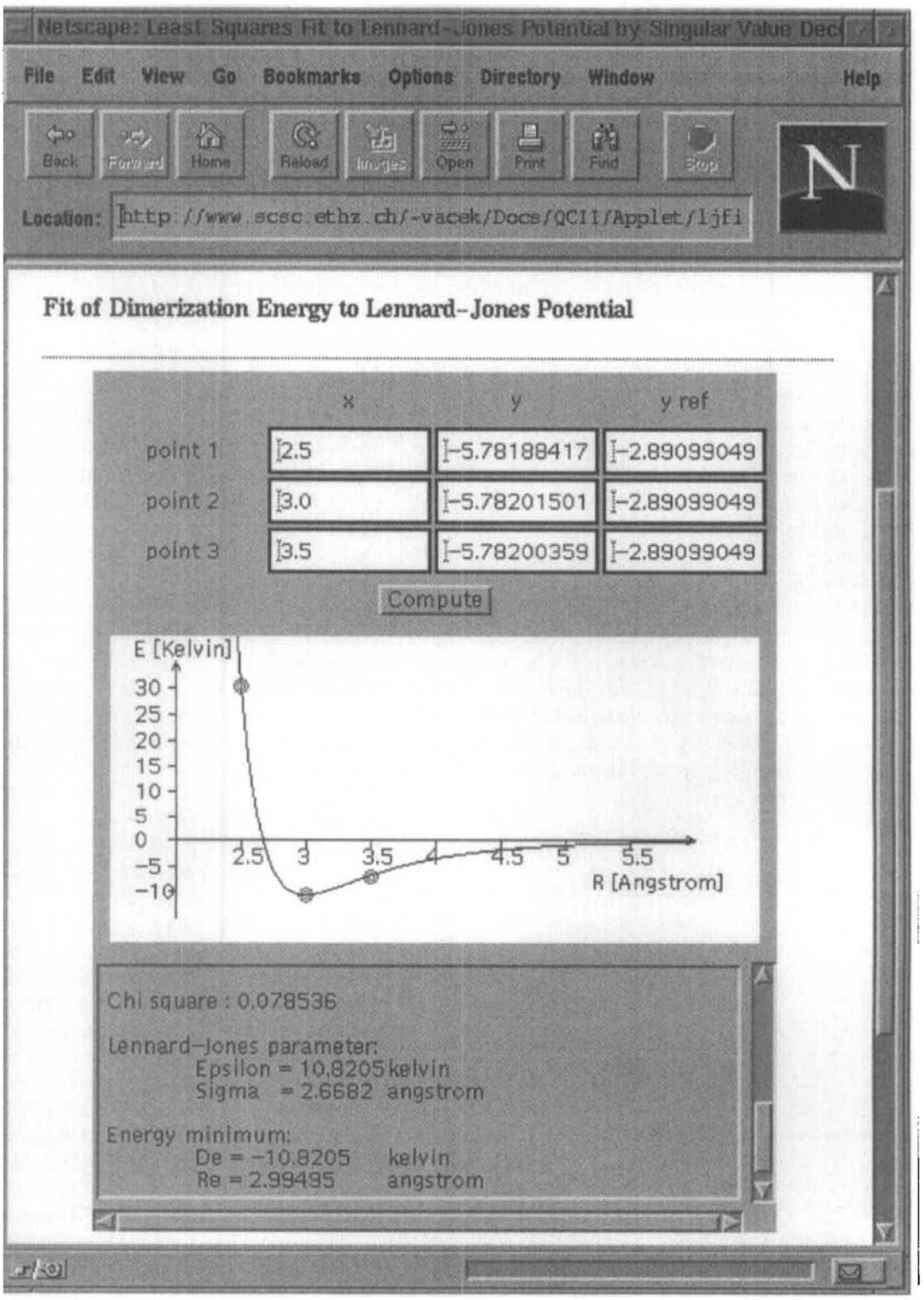

Fig. 2. *The Java applet of Exercise 6 fits a* Lennard-Jones *potential to a set of energy points determined for the helium dimer.* The students fill in the input data and select the compute button to obtain the fitted potential-energy curve and the output parameters.

applied to chemistry- and physics-related topics can be found at 'Gamelan: The Official Directory of Resources for Java' [18].

Web-based execution is important to the 'world-wide' distribution of these practical exercises, primarily because the data-processing programs are then as platform independent as the Web pages themselves.

4.1. *Web-Based Execution: Java Applets*

Java is a high-level object-oriented programming language which is specially fit for networking applications, because it contains classes which allow network access, handling of multimedia objects like audio clips and images, multithreading, *etc.* As an important result, one can write applets, *i.e.* applications which run inside a Web page. Code which has been written in Java is initially 'compiled' (or translated) into a very compact binary byte stream. This *machine-independent* byte stream is downloaded over the WWW along with the Web page and is interpreted locally by a Java interpreter within the browser.

Thus, the installation is very simple. All it needs are the HTML files and the byte streams of the embedded applets. However, the applications (in our case, originally written in another high-level language) need to be ported entirely to Java. Furthermore, for security reasons, since the program is executed on the client, the generated data cannot be saved in a database on the server.

An example which handles all data processing entirely within a Java applet is in Exercise 6, Van der Waals *Interactions*

(*vide infra Sect. 5.6*), which fits a *Lennard-Jones* potential to a set of energy points. The applet (see *Fig. 2*) consists of: a graphical user interface that lets the student modify the input data, the computation classes that perform the approximation based on singular-value decomposition [19], and a graphical output that displays results both numerically and as a curve.

4.2. *Web-Based Execution: CGI Binaries*

The CGI standard (Computer Gateway Interface) [20] defines how a browser can communicate with the server from which the HTML document was downloaded (see *Fig. 3*). CGI binaries are simple executables (or scripts) which read from standard input and write to standard output and which reside on the Web server in special Web-accessible directories. When the browser on the client sends data, the information is received by the HTTPd (HyperText Transfer Protocol daemon) [21] which starts the CGI binary. The CGI binary, since it runs on the server machine, can execute any application program available there. It can also write to disk, thus offering the possibility to create a database on the server. This makes communication of results among users easy and even enables collaborative work over the WWW.

This method has the advantage that there is no need to port (or even adapt!) the code which does the processing, and yet it can be run by anyone with WWW access and one can have a nice depiction of results. It is possible to create and share a base of collected output (*i.e.*, the students can compare with the results of other students). However, the installation is quite complex: in addition to the HTML file and the applets for in- and output, the CGI script must be installed as well as an executable that transforms from CGI standard to plain text, and, finally, the data processing executable itself. This, of course, has ramifications for maintenance as well as initial installation.

A typical example of such a setup is Exercise 7, *Rotation-Vibration Spectrum of HCl* (*vide infra Sect. 5.7*). The GUI which lets the student modify the input parameters is written in Java, but the processing is executed on the server *via* a CGI binary rather than within the browser. The Web page contains another Java applet for graphical display of the results (see *Fig. 4*).

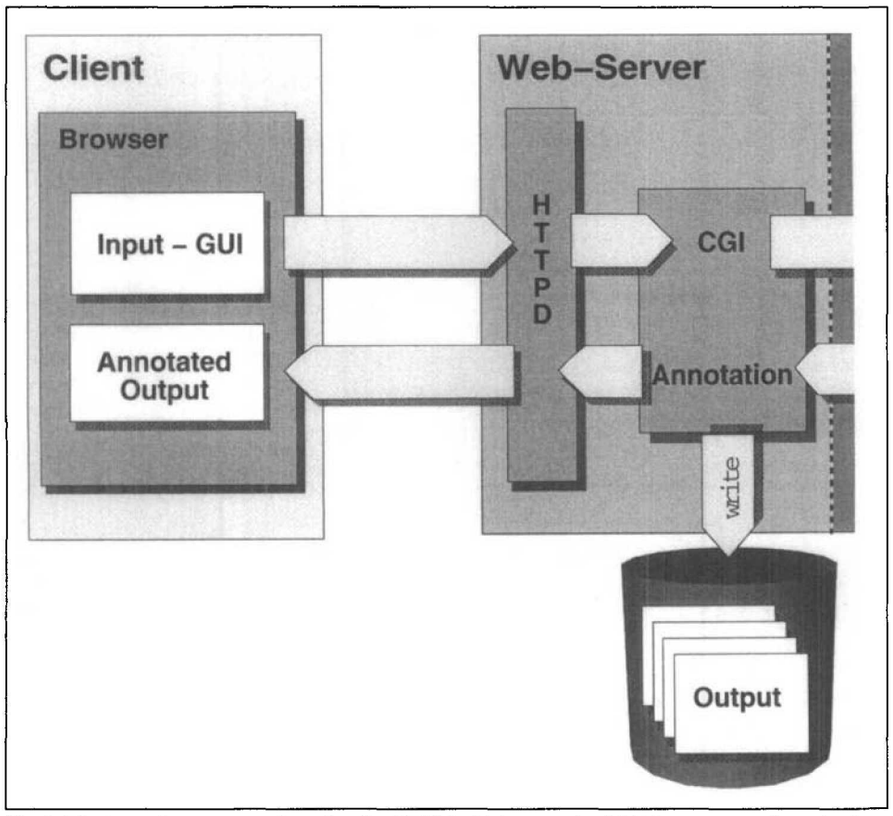

Fig. 3. *The input data are transferred to the HTTPd which starts the CGI binary to transform the data into the format requested by the application.* The (unmodified) application is executed with these data and the results are sent back *via* the CGI binary (which can also annotate and save them).

5. The Assignments

In this section, we provide a brief overview of the practical exercises. More complete descriptions of their content and the strategy behind their design can be found in other publications [3][4]. While reading this section, please refer to the *Table* and *browse the actual assignments* starting at `http://www.scsc.ethz.ch/chem/qcii.html`. As examples, printouts of some Web pages are provided (*Figs. 1*, 2, and *4*).

5.1. *Getting Started*

In this exercise, we introduce the features of the quantum-chemistry user interface and demonstrate how to build interactively a molecule by using the molecular builder. Options to customize the environment, like display options or launch options are set. The various building and editing tools of the GUI as well as the data-management mechanism are presented. By 'playing around' with the quantum-chemistry user interface, the students become familiar with the software environment and learn the basic skills for further lessons.

5.2. *Compute and Analyze*

The different setup steps of an *ab initio* calculation are illustrated for the simple example of formaldehyde and the formaldehyde ion. Steps proceed through input setup, job submission, monitoring, and output analysis. This exercise also shows the connections to the more chemical aspects of the problems, since the theoretically generated data is compared to the experimental results. The students find correlations between the size of the basis set, the level of electron correlation, the accuracy of the results, and the CPU time.

5.3. cis-trans *Isomerization of Glyoxal*

The students optimize the *cis-* and *trans*-equilibrium structures of glyoxal at the *Hartree-Fock* minimal-basis-set level of theory. They also optimize the transition-state structure that connects them to evaluate the barrier of rotation. The students learn the basic skills needed to optimize structures of simple organic molecules. Emphasis is placed upon using second-derivative analysis to determine the nature of stationary points.

5.4. *The Water Dimer*

The equilibrium structure of a hydrogen-bonded system, the H_2O dimer, is evaluated. Scanning the potential-energy surface (PES) for more stable structures than the accepted global minimum (which

shows only a single hydrogen bond) is encouraged [22]. The pitfalls of *basis-set superposition error (BSSE)* and the necessary correction for BSSE [23] are demonstrated using this example where the correction is greater than the observable, namely the hydrogen-bonding energy. This is the first time the students are working on an example which is of current research interest and which illustrates the interaction of computation and experiment [22][24].

5.5. Woodward-Hoffmann *Rules*

Considering the dissociation reaction $CH_2{=}O \rightarrow CO + H_2$, the HF molecular orbitals (MOs) of the reactants and products are analyzed under symmetry arguments. *Woodward-Hoffmann* MO diagrams are drawn out for C_{2v} and C_s symmetry, showing that the reaction is forbidden under C_{2v} symmetry, but C_s symmetry-allowed. The transition state is then optimized and confirmed to be of C_s symmetry. Furthermore, the 1,2-hydrogen-shift reaction of formaldehyde is explored. Students learn to appreciate the *Woodward-Hoffmann* rules as a selection mechanism for starting geometries for transition-state structure searches.

5.6. Van der Waals *Interactions*

The *van der Waals* interaction energy of the helium dimer at different interatomic distances is computed (eventually at several levels of theory). A numerical fit of the *ab initio* energies to the *Lennard-Jones* (LJ) potential to determine the parameters e and s of the LJ potential reveals the values for r_e and D_e. This fitting program is directly included into the HTML lesson assignment (see *Fig. 2*) as a Java [16] applet (*vide supra Sect. 4.1*). Using the LJ parameters, the structure and energy of the helium trimer is first predicted and then calculated. Differences between the expected and calculated values reveal the effect of the three-body interaction term. The students are made aware of the fact that the interaction between He-atoms is an up-to-date topic in computational chemistry [25].

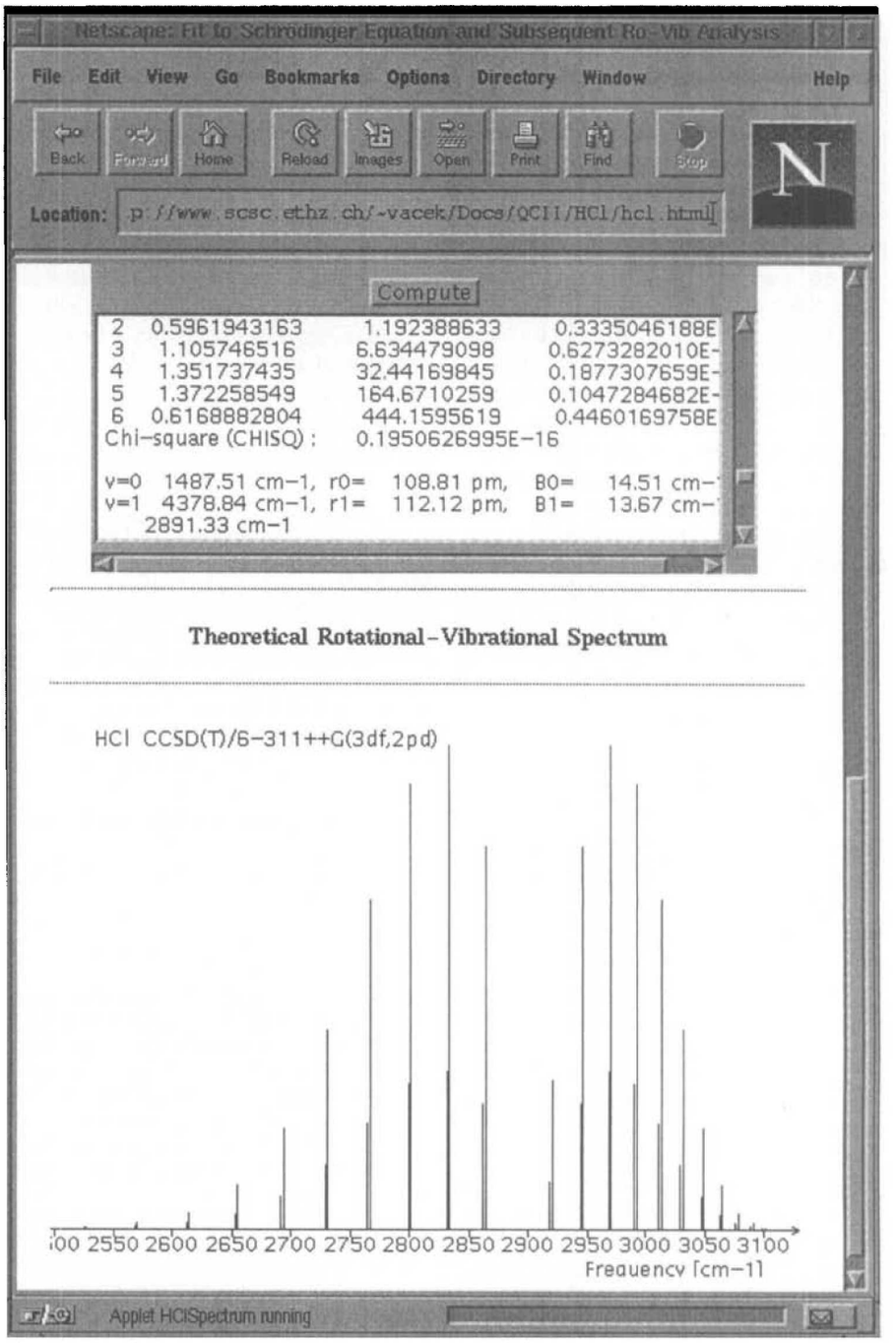

Fig. 4. *The rotation-vibration spectrum of HCl^{35} and HCl^{37} in Exercise 7 is based upon the numerical fit results from a CGI binary*

5.7. *Rotation-Vibration Spectrum of HCl*

In this exercise, we show how spectroscopic data can be derived from a potential-energy curve determined by *ab initio* techniques (see *Fig. 1*). In particular, we look at the rotational fine structure of the n_{01} fundamental adsorption of HCl. Here, we show the effort required for *ab initio* results to match the *quantitative* accuracy of experimental results. The only *ab initio* data items computed are points on the potential-energy curve. All other quantities are obtained by solving the nuclear *Schrödinger* equation for the said potential and by applying a rigid-rotor formalism. This data analysis (see *Fig. 4*) is done using the utility program incorporated directly in the Web page (*vide supra Sect. 4.2*). Results generated with the utility program can also now be archived for later retrieval by other students. This means that results from many levels of theory become available for comparison.

5.8. *Thermochemistry: Heat of Reaction*

In this exercise, we determine the heat (enthalpy) of reaction for the gas-phase reaction $C_6H_6(g) + 6\,CH_4(g) \rightarrow 3\,C_2H_4(g) + 3\,C_2H_6(g)$. The results computed can be matched against experimental heats of formation taken from thermochemical handbooks. The extrapolation to r.t. requires thermal corrections for translational, rotational, and vibrational degrees of freedom. These corrections which amount to several kcal/mol (*i.e.*, significant con-

tributions that must be considered for accurate results) are taken using the approach of ideal gasses of rigid rotors and harmonic oscillators.

5.9. *Thermodynamics and Kinetics*

Transition-state theory is employed to compute the equilibrium constant and the rate of reaction for $CH_3 + H_2 \rightarrow CH_4 + H$. For this purpose, the students must optimize the structures of the molecules involved, compute the vibrational frequencies, localize the CH_5 transition state, and evaluate partition functions. Reaction path following [26] is used to characterize and visualize the transition state and the energy profile of the reaction coordinate. Once, this energy is profile known, `TheRate` [14] is used to go beyond simple transition-state theory and to account for tunneling effects. The Web pages are not modified to our format but left in original form to emphasize the ease with which additional modules can be linked.

6. Experiences and Future Developments

The main goal of this class, namely the generation of the skills needed to use quantum-chemistry calculations to solve chemical problems, was achieved. The concept of relating computed data with experimentally observed results was an excellent approach to build that expertise. Furthermore, by addressing up-to-date chemical problems, we ensured that the students are exposed to current topics in computational chemistry. The overall experience made with the assignments, the format, and the software environment was also very positive. The HTML-formatted assignments greatly helped to increase the efficiency of the class. In the assignments, we will continue to incorporate reference links to online journals, manuals, databases, and related Web sites as they become available. We are also extending our documents by developing new features, including applets. For instance, we have recently completed the ability to archive processed results directly from the Web page, so that future students can benefit through studying results generated by previous students. The next steps regarding the enhancement of the assignments will be the completion of the current series which is biased towards the computation of 'spectroscopic data' (*vide supra* the *Table*). Specific topics which we would like to include are UV/VIS and NMR properties. We are discussing the generation of another set of assignments which is aimed at aspects of molecular modeling.

It seems that the WWW will act as an *open market* for the development and exchange of educational materials. Initiatives such as Australia's ACCVIP [10] and ETH-Zürich's NET [11] will foster such activities. More important, however, is the fact that, if standard rules of market will apply, then the materials available on the WWW will cover a broad range of areas at a high level of quality. Chemistry educational information on the Web is certainly growing in both quantity and quality, as much of it is developed by individuals dedicated to chemistry education.

This work was supported by the *Schweizerischen Nationalfonds* (Project No. 20-40838-94), the *Swiss Center for Scientific Computing* (SCSC), and by *Silicon Graphics' European Chemical Technology Center* in Basel. We are also indebted to Profs. *T.-K. Ha* and *W. Klopper* for their contributions to the practical assignments. Java, JavaScript, HotJava, UniChem, and Netscape are all trademarks of their respective holders.

Received: December 12, 1996

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