Reviews in Computational Chemistry 26

Edited by

Kenny B. Lipkowitz
Thomas R. Cundari

Editor Emeritus

Donald B. Boyd

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Preface

Earning tenure at an academic institution and running a steeplechase race successfully have a lot in common. Both require extensive training before the event begins, both involve hurdles to overcome and pitfalls to avoid, and both are grueling events that inevitably lead to a few twisted ankles or broken marriages. Unlike the steeplechase race where there exists a single winner (second place is considered "first loser"), multiple winners can be found in the tenure race, however.

Tenure decisions are often based on some institutionally defined, linear combination of teaching, research, and service to the community. However, not all institutions share the same values, nor do they have the same goals. While some institutions focus mainly on teaching and others focus primarily on research, they all share the common theme of ensuring that competent and caring teachers are interfacing with their students.

For those colleges and universities that emphasize research in the tenure portfolio, another common theme is that they all *want* their new hires to be successful in their research endeavors. This usually means providing reduced teaching loads for those new faculty during the first academic year, assigning mentors to oversee new faculty teaching and/or research strategies so as to help them avoid pitfalls that might derail an otherwise successful career, and providing startup funding so that those new faculty members can obtain the requisite equipment, supplies, and personnel needed to jump-start their research careers.

One often hears, anecdotally, how much a particular institution paid in startup funding to attract a highly regarded candidate to accept its offer in lieu of one from a competing institution. Sometimes those funds include valuable but inflationary content such as laboratory renovation costs, machine time fees, repair shop costs, partial summer salaries, and so on, which, superficially, balloon the startup costs to the point of extravagance. So, what are the startup packages in academic laboratories nowadays, and, are those packages really as extravagant as some are saying? Moreover, with respect to the readership of this book series, how do computational chemists fare with respect to experimentalists in this regard?

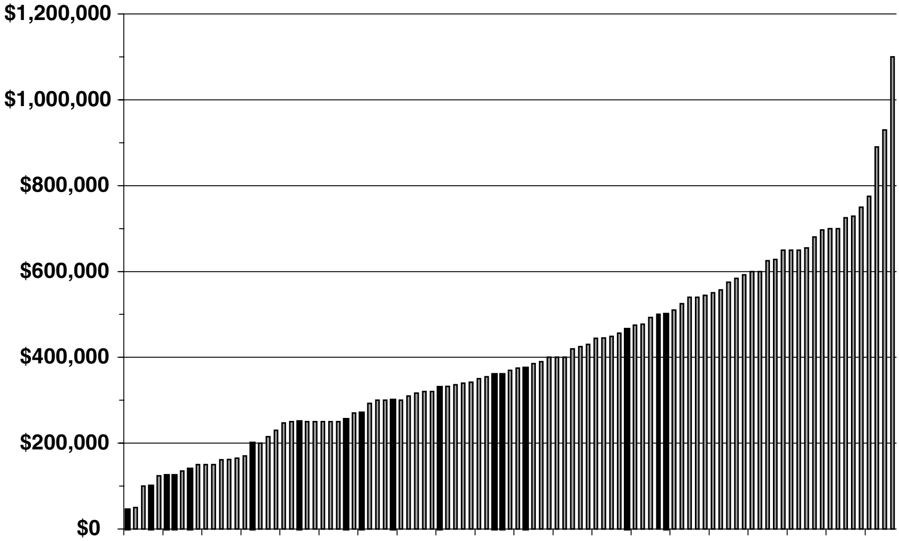

Figure 1 Representative set of startup packages provided by American chemistry departments in doctoral-granting institutions during the 2006–2007 academic year. Black lines are for computational chemists.

Some of these questions can be answered with data provided by the American Chemical Society's Petroleum Research Fund (PRF). The PRF asks new faculty members applying for a grant to delineate startup costs along with other information such as space allocations, teaching loads, etc. Figures 1 and 2 contain a random selection of startup packages during the 2006–2007 academic year. These plots show the data (sorted by increasing amount) for approximately 100 new investigators applying from universities with doctoral programs (Figure 1) and 45 new investigators from BS and MS granting institutions (Figure 2). Note that the scales are NOT the same in these figures, with doctoral institutions, providing significantly more research startup funds than do primarily undergraduate institutions, as expected.

The data in these plots are for Chemistry Departments only; excluded are data from engineering, geology, and physics departments (data for new investigators in the fields of chemical biology were not available). Parenthetically, chemists do significantly better in terms of their startup packages than do the people in these excluded groups, but this is a topic for another day. Also omitted are startup packages from non-American institutions because, frequently, one ends up comparing apples versus oranges in this regard.

The data depicted include real dollars made available for new investigators at American chemistry departments to use as they feel would be best for their research careers. Removed from these numbers are the costs of laboratory renovations and other such obligatory spending by an institution, as well as "in-kind" funds such as nuclear magnetic resonance (NMR) or

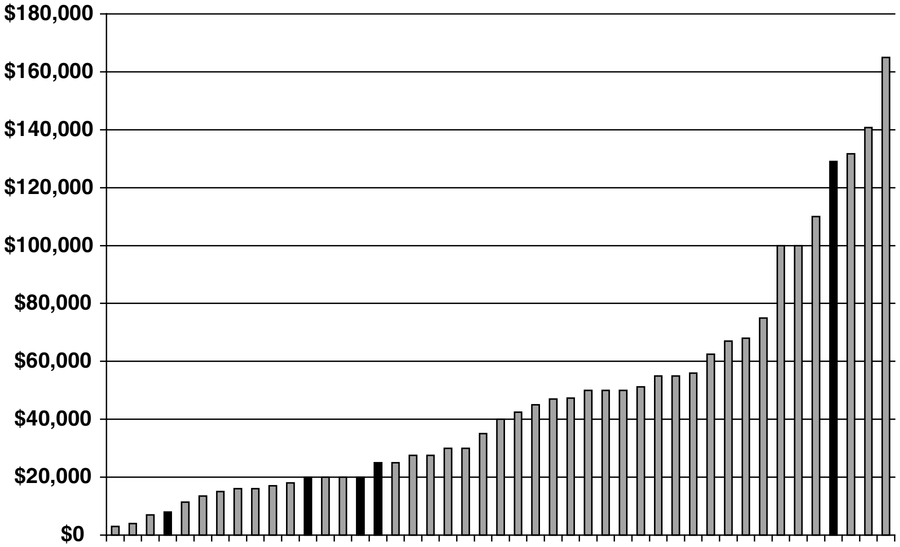

Figure 2 Representative set of startup packages provided by American chemistry departments in BS- and MS-granting institutions during the 2006–2007 academic year. Black lines are for computational chemists.

computer time, glass and machine shop time, and so on, each of which are desirable and meant to help the new faculty member but that were removed nonetheless because not all new faculty would think to put this kind of information into their PRF grant application. Also removed were summer salaries, travel monies, months of teaching assistant (TA) support, new journal costs, and other types of support that is already earmarked by a department for a particular use. What remains, then, is a noninflated, barebones, startup package that the new faculty member can use for what he or she thinks will best ensure success for the research component of his or her tenure portfolio. The data provided here, then, represents a lower bound on the level of support given by American institutions.

While some doctoral institutions are providing startup packages in excess of $800,000, most are giving $600,000 or less. Is this extravagant or is this necessary? The answer to that question clearly depends on the expectations each of those institutions have for their faculty, but also on their ability to provide those funds, especially when two or three new faculty are being hired in the same year (many institutions spread out their startup costs over 2–3 years). Given the cost of glassware, solvents/chemicals, spectrometers, chromatographs, and research assistantship line items, we will let you decide if these startup packages are reasonable or extravagant.

The undergraduate/MS-level schools can, in some cases, rival some of the doctoral program startup packages, but their packages are significantly less than those provided by doctoral institutions in general. Some institutions provide more than $100,000, but the majority of them provide startup packages between $20,000 and $75,000 (it is not clear if these funds are to be used exclusively for research or if they are intended also for teaching/curriculum development). Nonetheless, a clear gradation in research support exists for both undergraduate and doctoral institutions alike.

What is surprising and somewhat disconcerting is that computational chemists are given far fewer startup dollars to jumpstart their careers than is given to experimentalists. A decade ago a Silicon Graphics workstation with dual processors cost about $25,000, a cost that was comparable to a liquid chromatograph. One can argue that chromatographic columns are costly (some columns were typically $1500 each and prone to easy degradation), as are the costs for high-purity solvents to justify more funding for the experimentalist, but, that chromatograph would likely last for 10–15 years with proper maintenance while the workstation would be outdated and in need of replacement every 3–5 years. One might also argue that the computational scientist could use departmental or school computing resources (if they exist) or perhaps receive a user's grant from a nationally funded supercomputing center, but, that does not obviate the fact that experimentalists usually have access to expensive department-provided resources such as NMR and mass spectrometers. What is not arguable, however, is that the costs of hiring a postdoctoral researcher to get any new faculty member's research going on a fast track is exactly the same for computational chemists as it is for experimentalists at a given institution, yet it appears, on the whole, that computational scientists are being short changed in their startup packages. This is an issue that senior computational chemists need to pay attention to and insist, when new hires are made, that theorists be treated on the same footing as experimentalists. The irony in all this is that a disproportionate number of computational chemists are cited heavily in the scientific literature compared to researchers in other disciplines. Indeed, in the preface of Volume 13 of this book series, we carried out a thorough assessment of citation trends and pointed out that 25% of the top-cited chemists are computational scientists, even though computational chemists constitute only about 5% of all chemists. Despite the shortcomings associated with less funding for computational chemistry than for experimental chemistry, we can say that computational chemists, as a group, are doing more than their fair share of having an impact on science.

Because computational chemistry is so important in today's laboratory setting, we know that many experimentalists want to use the theories and the associated software developed by computational scientists for their own needs. The theoretical underpinnings and philosophical approaches used by theorists and software developers are often buried in terse mathematics or hidden in other ways from the view of a traditional black-box-using bench chemist who has little time to become truly proficient as a theorist, or who might stumble into some theoretical pitfall that would detract from the explanations of their scientific findings. Yet, those experimentalists want very much to use computational tools to rationalize their results or, in some instances, to make predictions about what next to do along their research trajectory. Because of this need we started the *Reviews in Computational Chemistry* book series that, in hindsight, could just as well have been called "Tutorials in Computational Chemistry."

Because the emphasis of the material covered in this book series is directed toward the novice bench chemist wanting to learn about a particular method to solve his or her problems (or for that matter, the seasoned veteran computational chemist needing to learn a new technique with a modicum of effort), we have again asked our authors to provide a tutorial on the topic to be covered in that chapter. As before, they have risen to the occasion and prepared pedagogically driven chapters with the novice in mind.

We begin this volume with a tutorial on quantum mechanical calculations of noncovalent π interactions because of their significance in directing crystal packing, supramolecular assembly, protein folding, drug binding, and the like. These interactions, especially π stacking of aromatic rings in the domain of organic and biological science, have a history of being perplexing to understand and difficult to assess numerically because they are generally weak interactions and they compete with other kinds of stabilizing interactions. In Chapter 1 C. David Sherrill outlines the challenges for computing π interactions by describing the problems associated with computing those interactions. He describes the application of robust electronic structure methods to compute π interactions reliably and reliable approximations one can make for speeding up the calculations. Covered are electron correlation and basis set requirements, counterpoise corrections, and additive basis/correlation approximations. The emphasis in this tutorial is on the prototype of aromatic π–π interactions, the benzene dimer. Many of the traps one could fall into with modern commercially available software are uncovered and revealed for the novice in the first part of the chapter. In the second part of the chapter the author explains how one can reduce computational costs while still maintaining a reasonable degree of accuracy. Described are truncated basis sets, Pauling points, and resolution of the identity, along with spin-component-scaled second-order Møller–Plesset (MP2) and explicitly correlated R12 and F12 methods to accelerate convergence to the complete basis set limit. Sherrill ends the tutorial by focusing on symmetry-adapted perturbation theory to compute the individual components of intermolecular interactions, e.g., electrostatic, induction, dispersion, and exchange repulsions, so that a rational framework can be constructed for describing the binding of even simple systems such as the benzene–toluene sandwich complex.

Gregory S. Tschumper expands on this topic in Chapter 2 where he describes ab initio and density functional calculations for weak, noncovalent interactions in clusters. Following an introduction that defines the scope of the chapter and a historical perspective of the nature of weak interactions, the author provides a tutorial for the novice on fundamental concepts with a simple model system consisting of cyclic hydrogen fluoride molecules (trimer, tetramer, and pentamer). The rigid monomer approximation and supermolecular dissociation and interaction energies are described first, followed by a pedagogical section on counterpoise corrections for treating basis set superposition errors. Two-body approximations and cooperative/nonadditive effects are defined and described. Higher order cooperative effects are also described and a many-body decomposition scheme for weakly bound clusters is explained in detail with an application to hydrogen fluoride (HF) clusters. Because energy is an extensive property, a pedagogical section on size consistency and extensivity is provided for the reader. A section on high-accuracy computational strategies is then presented, beginning with a primer on electron correlation and a primer on atomic orbital (AO) basis sets that includes extrapolation methods and explicitly correlated methods. Linear scaling methods are described and a tutorial on estimating E_{int} in the CCSD(T) CBS (complete basis set) limit is given. The author balances this with a section on less demanding computational strategies using MP2 and density functional theory (DFT) techniques. Other computational issues are brought to light and illustrated with results from calculations on water clusters. Aspects of computing geometries and vibrational frequencies for noncovalent clusters are presented.

The theme of quantum mechanics is continued in Chapter 3 where Peter Elliott, Filipp Furche, and Kieron Burke describe how to compute excited-state properties using time-dependent density functional theory (TDDFT). Ground-state DFT has become the de facto standard, especially for chemists, biologists, and materials scientists for predicting ground-state properties of molecules, but it cannot in its typical implementation treat electronic excitations. TDDFT can be used to do this, and here the authors provide a state-of-the-art overview of the method. They begin with a review of the ground state covering the formalism, approximate functionals, and basis sets, and then introduce time-dependent theory. Here the Runge–Gross theorem is explained, Kohn–Sham equations described, and linear response to external fields is presented. While formally exact, a TDDFT calculation also requires an approximation for the exchange–correlation (XC) potential, and those approximations are then introduced. With that background the authors describe the implementation of TDDFT and the basis sets used commonly nowadays, using as an example the naphthalene molecule. That section is followed by one that assesses the performance of TDDFT, using naphthalene as an example. The authors examine the influence of the ground-state potential, the influence of the XC kernel, the errors in potential versus kernel, and then they describe how to understand linear response TDDFT. Also included in the chapter is a close look at how well TDDFT performs for noble-gas atoms. The authors then take a look beyond standard functionals by examining double excitations, polymers, solids, and charge-transfer systems. The chapter ends with coverage of topics where TDDFT is being applied and where development goes beyond simple extractions from linear response theory.

The theme of quantum mechanics is again continued in Chapter 4 where Thomas Vojta provides a tutorial on quantum phase transitions. Understanding and describing phase transitions is important because of their ubiquitous nature and how they shape our world. The phase transitions that most of us are aware of take place at nonzero temperature where, for example, the ordered state of ice becomes less ordered water at the melting point or where iron loses its ferromagnetic character at its Curie point to become paramagnetic. Attention has now shifted to the study of another type of phase transition that occurs at zero temperature and is induced by nonthermal parameters such as pressure, magnetic field strength, or even chemical composition. Thus, at an applied magnetic field strength, of about 5 T, $LiHoF_4$ undergoes a phase transition from a ferromagnet to a paramagnet; one can envision the impact that such transitions have in defining magnetic, optical, and electrical properties of materials that technologists will soon employ to make advanced products for consumption. The purpose of this chapter is to introduce the theory of quantum phase transitions, showing similarities to and differences from typical thermal transitions that most of us are more familiar with and to point out the computational challenges presented by quantum phase transitions and successful approaches used to meet those challenges. Vojta begins by describing phase transitions and critical behavior. Landau theory, scaling, and renormalization group theory, finite-size scaling, and quenching disorder are then covered. Then, classical versus quantum phase transitions are described including quantum scaling and quantum-to-classical mapping, going beyond the Landau–Ginzburg–Wilson paradigm, and impurity quantum phase transitions. There exist formidable challenges to computing quantum transitions, which are explained clearly by the author. Also covered in this chapter are the classical Monte Carlo (MC) approaches, including the simplest models displaying quantum phase transitions—the quantum Ising model in a transverse field, the dissipative transverse-field Ising chain, and other such methods. This is followed by a discussion of quantum Monte Carlo approaches to the problem, including the world-line MC algorithm and the stochastic series expansion algorithm. The chapter ends with a brief overview of other computational approaches to quantum phase transitions.

We continue in the ensuing chapters with several tutorials tied together by the theme of how to exploit and/or treat multiple length scales and multiple time scales in simulations. In Chapter 5 Thomas Beck introduces us to real-space and multigrid methods used in computational chemistry. Real-space methods are iterative numerical techniques for solving partial differential equations on grids in coordinate space. They are used because the physical responses from many chemical systems are restricted to localized domains in space. This is a situation that real-space methods can exploit because the iterative updates of the desired functions need information in only a small area near the updated point.

A problem with this approach, however, is that the solver tends to stall due to the long wavelength components of the errors if the iterations are performed on only a single, fine grid. Multigrid methods overcome this problem by using information from a range of length scales. In this tutorial Beck gives us a few examples of where such computational methods can be used and then introduces us to the basics of representing partial differential equations in real space. Two of the most basic and useful equations used by computational chemists and engineers are considered: the Poisson equation and the Schrödinger equation. Finite-element representations, finite-difference representations, iterative updates of functions, and limitations of real-space methods for a single, fine grid are described. Multigrid methods are then introduced and explained in a pedagogical manner. Because eigenvalue problems are more difficult to solve than those encountered in solving the Poisson equation, a section is dedicated to this. Thereafter, treatments for nonlinear scaling for electronic structure calculations are described. Other nonlinear problems such as solving the Poisson–Boltzmann and Poisson–Nernst–Planck equations are then introduced and explained. The author provides some tips and advice about writing multigrid solvers and then provides a literature review of applications in chemistry, biophysics, and materials science. The chapter ends with a listing of real-space and multigrid codes for use in the areas of electronic structure, electrostatics, and transport, and speculation on research directions that may be pursued in the near future.

In Chapter 6 Francesca Tavazza, Lyle E. Levine, and Anne M. Chaka provide a tutorial on hybrid methods for atomic-level simulations that span multiple length scales in the solid state. To examine the mechanical behavior of materials, one needs to account for bond making/breaking, atom rearrangements, or defect properties using simulation techniques on the atomistic, nanoscale, but, one also needs to account for micro- or macroscale phenomena such as long-range stress fields that cover hundreds of nanometers and larger. Because one cannot yet simulate macroscopically large systems with atomic-level resolution, the use of hybrid technologies is commonly implemented where different length scales are simulated simultaneously in a coupled fashion. The main obstacle to overcome is the development of efficient and physically correct coupling schemes. The interface between different computational models is a region that is sometimes called the "handshake" region where nonphysical forces (ghost forces) can arise due to the intrinsically different interaction range associated with each of the computational models employed and where, for hybrid methods that deal with dynamical processes, wave reflections can occur at artificial boundaries. In this tutorial the authors divide the methodologies into two main classes: those dealing with coupling classical atomistic models to continuum models and those coupling classical atomistic models to quantum models. In the section on atomistic-continuum coupling the authors begin with zero temperature equilibrium methods including FEAt (finite-element coupled with atomistic modeling), the quasi-continuum (QC) method, the coupled atomistic and discrete dislocation method, the atomic size finite-element method, and Green's function boundary condition methods. Finite-temperature equilibrium methods are then discussed including the QC-free energy functional method, the quasi-continuum Monte Carlo method, and others before turning to hybrid methods used to explore the dynamical evolution of systems composed of a continuum region. These systems are usually described with finite-element methods coupled to a discrete-described region that is usually modeled with molecular dynamics algorithms implementing classical potentials. Domain decomposition methods, adaptive model refinement techniques, coarse-grain molecular dynamics, and boundary conditions methods are introduced and then described in a straightforward manner. The second half of the tutorial involves the coupling of classically described domains to quantum mechanically described regions. Static and semistatic methods are described along with the first-principles Green's function boundary condition method and the quantum atomistic static interface method. Then the authors describe dynamics methodologies including the coupling of length scales method, the learn-on-the-fly method, and Ogata's method. The authors provide examples of applications of each method as they appear throughout the chapter. Also provided are easy to comprehend diagrams that illustrate what is being described.

The focus shifts in Chapter 7 from materials science to biology, but the theme remains multiscale modeling. In this chapter Alfredo E. Cárdenas and Eric Barth present a tutorial on extending the time scale in atomically detailed simulations. The authors begin by introducing the Verlet method and the potential functions used in molecular dynamics (MD) simulations. They then explain what multiple time step (MTS) methods are, and then they examine several such techniques. Cárdenas and Barth begin with the idea of splitting the forces that require different time steps for numerical resolution based on a simple distance parameter, and then they describe an alternative method of numerical integration with force splitting to deal with fast and slow components of the forces. An assessment of limitations on the size of the time steps allowed is presented before Langevin dynamics is introduced. Then a MATLAB-based tutorial is presented on impulse and extrapolation MTS methods. While MTS methodologies can extend simulation time scales somewhat, they are not useful for many applications such as examining large conformational changes in proteins. Accordingly, the authors introduce a different approach to extending the time scale that involves techniques that are generally referred to as "path methods." This includes transition path sampling, maximization of the diffusive flux (MaxFlux), discrete path sampling with the string method, and optimization of action. The latter path method described by the authors emphasizes the stochastic difference equation in length (SDEL). Here they use literature examples from the realm of biology such as protein folding, B-Z DNA transitions, and the like to make their point. An appendix containing MATLAB scripts for the tutorial is included.

The final chapter returns to the topic of materials science. In Chapter 8 Edward J. Maginn provides a historical account of atomistic simulations of ionic liquids, especially room temperature ionic liquids (RTILs). After defining what RTILs are, he provides a short (pre)history of computational efforts in this field. Then, in a didactic fashion, Maginn reviews the history of early simulations by first introducing the potential functions used, then assessing the limitations of those functions, and, finally, examining sampling issues associated with simulations of this class of liquids, which differ (electrostatically) from most traditional liquids that have been studied to date. With that background Maginn delves into more refined models for RTILs focusing on how best to compute structures, energies, properties such as heat capacities, Henry's law constants, and other issues related to solubility in ionic liquids. Of particular note, especially for novices, are the implications of slow dynamics of RTILs when computing transport properties. Because of this potential "road block," the author presents a full section dedicated to this topic. That section is followed by one on computing macroscopic properties such as self-diffusivities, viscosities, electrical conductivities, and thermal conductivities of ionic liquids. Compared and contrasted are equilibrium and nonequilibrium methods used for calculating these properties. Coarse-graining techniques and ab initio MD methods are then described. Finally, Maginn takes the novice modeler through a tutorial on how to carry out an RTIL simulation. This tutorial contains an ample selection of "Do's and Don'ts" associated with the selection of codes one might use, the choice of force field to implement, how to analyze the data derived from the simulations, and the use of operating systems and parallel computing for large-scale atomistic simulation.

Reviews in Computational Chemistry is highly rated and well received by the scientific community at large; the reason for these accomplishments rests firmly on the shoulders of the authors we have contacted to provide the pedagogically driven reviews that have made this ongoing book series so popular. To those authors we are especially grateful.

We are also glad to note that our publisher now makes our most recent volumes available in an online form through Wiley InterScience. Please consult the Web (http://www.interscience.wiley.com/onlinebooks) or contact reference@wiley.com for the latest information. For readers who appreciate the permanence and convenience of bound books, these will, of course, continue.

We thank the authors of this and previous volumes for their excellent chapters.

Kenny B. Lipkowitz
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Thomas R. Cundari
Denton

February, 2008

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