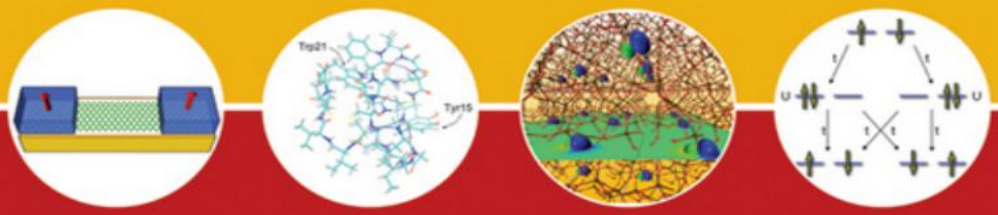
Computational Methods *for* Large Systems

Electronic Structure Approaches for Biotechnology and Nanotechnology



Edited by

Jeffrey R. Reimers

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To Noel Hush
who showed me the importance of doing things to understand the critical
experiments of the day and the need for simple models of complex phenomena,
and
to George Bacskay
who taught me the importance of getting the right answer for the right reason.

Preface: Choosing the Right Method for Your Problem

Computational methods have now advanced to the point where there is *choice* available for almost any problem in nanotechnology and biotechnology. In this book, the various methods available are presented and applications developed.

Given the difficulty in solving (relativistic) quantum mechanical equations for systems containing thousands of atoms, this situation is truly amazing and demonstrates the results of dedicated work by many researchers over a long period of time. Once demeaned by researchers as being useless for everything practical, computational methods have come into their own, providing fresh insight and predictive design power for wide-ranging problems: from superconductivity to semiconductivity to giant magnetoresistance to molecular electronics to spintronics to natural and synthetic polymer composition and properties to color design to nonlinear optics to energy flow to electron transport to catalysis to protein function to drug design.

Although much modern software is to be commended for its accessibility and ease of use, this advantage can be a luring trap. Electronic structure calculations on systems of any size are never simple. Many things can go wrong, and just because a method has always done the job in the past doesn't mean that it will continue to do so for a new problem that may appear very similar but which in fact embodies an additional unexpected effect. Proper understanding of the methods, including their strengths and weaknesses, is always essential. This book sets out to provide the background required for a range of approaches, containing extensive literature references to many of the

subtle features that can arise. Practical examples of how this knowledge should be applied are then given.

Amazing as progress has been, many significant problems in physics, chemistry, biology, and engineering will forever remain outside the reach of direct quantum mechanical electronic structure calculations. By no means does this mean that the technologies now available cannot be usefully employed to tackle these problems, however, and a significant part of this book is devoted to multiscale-linking methods. For example, the surfaces of most heterogeneous catalysts are extremely complex, and hundreds of chemical reactions may be involved. Applications of this type of problem include the combustion of fossil fuels, atmospheric pollution modeling, and many industrial chemical reactions and smelting processes. Natural and synthetic polymers present similar challenges. What existing electronic structure methods offer is the data to go into more complex, perhaps multiscale models of the phenomena. Other examples in quite different areas include protein folding, biological processes on the microsecond-to-second time scale, including the origin of intelligence, and long-range strong electron correlations in superconductors and other materials.

The fortunate position that we are in today is owed primarily to the development of density functional theory (DFT). This is the basic workhorse for electronic structure computations on large systems, being appropriate for biological, chemical, and physical problems. Part A of the book is devoted to the fundamentals of DFT, stressing the basics in Chapter 1 and then its two most common implementations strategies, atomic basis sets in Chapter 2 and plane-wave basis sets in Chapter 3. In the early days, atomic basis sets were designed to solve the burning issues at the time, such as the nature of the hydrogen molecule and the water molecule, while plane-wave basis sets could

tackle problems of similar difficulty, such as the structure of simple metals. Today, both types of methods can be applied to almost any problem, each with its own advantages and disadvantages. An important feature of Chapter 1 is that it describes not only traditional DFT for the ground state of molecules and materials but also modern time-dependent approaches designed for excited states and nonequilibrium transport environments.

Deliberately missing from this book is an extensive discussion of which density functional to use. This may seem a terrible oversight in a book that is really intended as a practical tool for a new science. DFT gives the exact answer if the exact density functional is used, but alas this is unknown and perhaps even unknowable. So what we now have is a situation in which computational programs can let the user select between hundreds of proposed approximate functionals, or even make a new one. However, from a practical perspective, the situation is not that bad. Only a handful of density functionals are in common use, with just 14 mentioned in this book (B3LYP, B97D, BLYP, BOP, BP86, CAM-B3LYP, LC-BOP, LDA, LDA+DMFT, LDA+U, PBE, PBE0, PW91, and SOAP), with the most commonly used functionals being B3LYP, LDA, PBE, and PW91. B3LYP is the most commonly used functional for chemical problems, owing to its inclusion of more physical effects, whereas PW91 and PBE are the most commonly used functionals in the physics community, as they are typically good enough in these applications and are much faster to implement.

A density functional is not a single unit but usually comes as a combination of various parts, each intended to include some physical effect. Choosing a functional that includes all of the physical effects relevant to a particular application is thus essential. In this book the applications chapters provide significant discussion as to which functionals are appropriate for common applications. Many specialized

functionals exist that are not discussed, so although the book describes what is good for most, experienced users should be aware that other attractive options do exist.

The most common physical effects included in modern density functionals are short-range correlation, short-range exchange, long-range correlation, long-range exchange, asymptotic correction, and strong correlation. All density functionals include short-range correlation and short-range exchange, with LDA including only these contributions and thus being one of the simplest and most computationally expedient functionals available. LDA gives the exact answer for the free-electron gas, a problem to which many simple metals can realistically be compared. When the nature of the atomic nuclei become important, this functional takes the wrong qualitative form, however. Nevertheless, it provides a useful point even in the worst-case scenarios and hence forms a simple and useful approach. It does not provide results of sufficient accuracy to address any chemical question, however, so its realistic use is confined to a few problems involving simple metals. The next simplest functionals improve on LDA by adding a derivative correction to the local correlation description and are generically termed generalized-gradient (GGA) approximations, with classic functionals of this type including BP86, PW91, and PBE. In general, GGAs provide descriptions that attain chemical accuracy and hence can be widely applied. Sometimes LDA provides results in better agreement with experiment than common GGAs, however, and researchers are thus tempted simply to use LDA. This is a very bad practice, as GGAs always contain more of the essential physics than does LDA, and what is required instead is to move to a more complex functional that includes even more interactions. Get the right answer for the right reason.

In widespread use for chemical properties are hybrid functionals such as B3LYP and PBE0, which include long-range exchange contributions in the density functional. This improves magnetic properties, long-range interactions, excited- and transition-state energetics, and so on. Such methods are intrinsically much more expensive than GGAs, however. Recent advances of great relevance to biological simulations include the development of density functionals containing long-range exchange, such as B97D, as is required to model dispersive van der Waals intermolecular interactions. As the exchange and correlation parts of the density functionals are obtained independently, physical constraints concerning their balance are not usually met, leading to errors in their properties at long range that become important for charge separation processes, extended conjugation, band alignment at metal–molecule interfaces, and so on. Modern functionals such as CAM-B3LYP and LC-BOP contain corrections that reestablish the proper balance, improving properties computed. Finally, approaches such as LDA+U provide explicit empirical corrections for the extremely short range, strong electron correlation effects that dominate the chemistry of the rare earth elements, for example, and are often relevant for metal-to-insulator transitions and superconductivity.

Over the next decade, the future for density functional theory looks bright. There is much current interest not only in developing corrections to account for the shortcomings of standard GGA-type functionals, but there is also keen interest in developing new classes of functionals that contain intrinsically the correct asymptotic properties for electrons in molecules. This should dramatically simplify functional design and implementation, making the use of DFT much easier for users.

Certainly the most significant issue with current implementations of DFT is that no systematic process exists

for improving functionals toward the illusive exact functional. This is where alternative computational strategies of an ab initio nature can be very useful. Part B of the book looks at methods that can be used when modern DFT just doesn't work. Historically, the most common ab initio method for electronic structure calculation has been Hartree–Fock configuration-interaction theory. This involves use of a simplistic approximation, that proposed by Hartree and Fock, followed by expansions that converge to or even explicitly determine the exact answer (within the basis set used). The Hartree–Fock approximation itself is about as accurate as LDA and is not suitable for studying chemical problems, but like LDA can provide good insight into the operation of more realistic approaches. Although codes exist that can in principle give the exact solution to any problem, in practice this can only be achieved for the smallest systems, certainly nothing of relevance to this book. As a result, some empirically determined level of truncation of the ab initio expansion is necessary (coupled to a choice of basis set, of course), making their practical use rather similar to that of DFT—always find out what works for your problem using model systems for which the correct answer is known. The coupled-cluster method provides the “gold standard” for chemical problems, often producing results to an order-of-magnitude higher accuracy than can be achieved by DFT, but at much greater computational expense. Nevertheless, how such methods can be applied to large systems of nanotechnological and biotechnological relevance is shown in Chapter 5. These methods fail for metals, however, and so are less popular in solid-state physics applications. They handle strong electron correlations properly and easily, of course, and how they may be combined with DFT to solve such key problems as those relevant to metal–insulator transitions and superconductivity, the combination allowing the strengths of

each method to be exploited while circumventing the weaknesses, is described in Chapter 6.

Hartree–Fock-based approaches will always scale extremely poorly as the system size increases, and an alternative ab initio method exists that scales much better while being applicable to molecules and metals alike: quantum Monte Carlo. The problem with this method has always been its startup cost, as even the simplest systems require enormous computational effort. But the time has now come where algorithms and computers are fast enough to solve many chemical and physical problems to a specifiable degree of accuracy. The method has come of age, and these advances are reviewed in Chapter 4. Because of the excellent scaling properties of this method, applications to larger and larger systems can now be expected to appear at a rapid rate.

But no matter how far computational methods such as DFT, configuration interaction, or quantum Monte Carlo methods advance, the researcher will hunger for the ability to treat larger systems, even if at a more approximate level. Part C of this book addresses these needs. Chapter 7 covers approximate but accurate schemes for implementing DFT and other methods that allow complex systems to be broken down into discrete fragments, achieving considerable computational savings while allowing chemical intuition to be used to ensure accuracy. Chapter 8 describes semiempirical Hartree–Fock-based approaches in which most of the interactions are neglected and the remainder parameterized, leaving a priori computation schemes that at times achieve chemical accuracy and are available for all atoms except the rare earths. A similar approach, but this time modeled after DFT, is described in Chapter 9. The DFT approach widely applicable to both biological systems and materials science but requires parameters to be determined for every pair of atoms in the periodic table, providing

increased accuracy at the expense of severe implementational complexity. It is now sufficiently parameterized to meet wide-ranging needs in biotechnology and nanotechnology.

Even so, some problems, such as superconductivity and the Kondo effect, require the study of electron correlations on length scales well beyond the reach of semiempirical electronic structure calculations. In Chapter 10 we look at a range of basic chemical models that describe the essential features of such systems empirically, leaving out all nonessential aspects of the phenomena in question. These methods follow from the analytical models used to put together the basics of chemical bonding and band structure theories in the 1930s–1960s, with the semiempirical methods described in Chapters 8 and 9 also originating from these sources. Accurate electronic structure calculations remain important, but in Chapter 10 we see that they only need to be applied to model systems to generate the empirical parameters that go in the electronic structure problem of the full system.

So, no matter what the size of the system, electronic structure methods are now in a position to contribute to the modeling of real-world problems in nanotechnology and biotechnology. Choosing whether to use empirical models parameterized by high-level calculations, use the DFT workhorse, or use methods that allow systematic improvement toward the exact answer is now a pleasant problem for researchers to ponder. Just because a certain type of problem has been solved historically by one type of approach does not mean that this is the best thing to do *now*. I hope that this book will allow informed choices to be made and set new directions for the future.

Part D presents applications of electronic structure methods to nanoparticle and graphene structure (Chapter 11), photobiology (Chapter 12), control of polymerization

processes (Chapter 13), nonlinear optics (Chapter 14), nanoparticle optics (Chapter 15), heterogeneous catalysis (Chapters 16 and 17), spintronics (Chapter 18), and molecular electronics (Chapter 19).

This book has its origins in the Computational Methods for Large Systems satellite meeting at the very successful WATOC-2008 conference organized by Leo Radom in Sydney, Australia. I hope the book captures some of the excitement of that meeting and the overwhelming feeling that we are now at the tip of an enormous expansion of electronic structure computation into everyday research in newly emerging technologies and sciences.

I have had a go at most things described in this book at some stage of my career, and can vouch for a lot of it. As for the rest, well, they are things that I always wanted to do! I hope that you enjoy reading the book as much as I have enjoyed editing it.

Color Figures

Color versions of selected figures can be found online at

ftp://ftp.wiley.com/public/sci_tech_med/computational_methods

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