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Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials

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Editor

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Foreword

Many powerful computer codes exist in the field of molecular chemistry, based on *ab initio* quantum-mechanical techniques. They can predict many properties of small- and medium-sized molecules with reasonable accuracy and at comparatively low cost. Their use has become common practice in the last ten years in many areas of activity, particularly in experimental chemical research, both in academic and in industrial environments.

The situation is much less advanced in the parallel field of condensed-matter studies. This is not due to a lack of potential interest: the development of new materials is one of the areas where the rate of progress is most rapid, and the amount of financial investment is largest. Materials for electronic and mechanical applications are in most cases crystalline structures, perfect or with controlled dosage of defects, whose properties cannot be understood without reference to an accurate description of the system at an atomic scale.

The intrinsic difficulty of handling systems of potentially infinite size explains only in part why crystalline studies are so far behind the current frontier of molecular quantum chemistry, a gap which presently is about fifteen years. Another possible reason may be that theoretical chemists have developed over many decades widely accepted interpretative schemes, a relatively standard language, a number of practical tools, good books and excellent computer codes so that having access to that technology does not require a very high-level entry point. On the other hand, making the wealth of knowledge embodied in standard solid-state theory compatible with an atomic-scale description of condensed systems is still an open problem. The question is how to transfer concepts and results from a "quantum-chemical" description of crystals to the parameterized world of solid-state physicists, and vice-versa.

Furthermore, the research and development effort which is being devoted to the implementation of powerful and user-friendly codes for the study of crystalline properties is curiously enough much less intensive than that devoted to the production of new molecular codes, and in the improvement of existing ones whose performance is already excellent. It is thus not surprising that the molecular cluster model, which can utilize standard codes with only minor modifications, is at present the favourite tool for quantum-mechanical investigations of the properties of crystals and their surfaces.

We now have the opportunity to change this state of affairs. There are a number of general-purpose, reasonably accurate and well-tested *ab initio* computer codes for crystals which are available to the scientific community. The rate of their improvement depends, in a sense, on their circulation, on the criticisms they receive and on the suggestions which are derived from their use. It is also very important that the various groups active in this field are open to unbiased comparison of the merits and drawbacks of their proposals, both as concerns basic ideas and approximations, and actual implementation of computer codes.

Schools and workshops can play a useful role to this effect, by teaching young people active in the field of Material Science how to exploit these new powerful tools. The present book contains the Proceedings of the **Fourth School of Computational Chemistry**, organized by the Interdivisional Computer Chemistry Group (GICC) of the Italian Chemical Society, and held in Torino on 19-24 September 1994, whose schedule is reported in Appendix A. Only the morning lectures (with few exceptions) are reproduced here, the afternoons being devoted to practical exercises performed by the students with use of the three codes available at the School, and described in Part 3.

The texts of the lectures can give only part of the information which can be obtained at a School through the possibility of practicing with the different programs, and from the contact with their authors. They nevertheless represent, on the whole, a useful introduction to the field, a reference for deeper study of certain specific subjects, and an objective body of information concerning the state-of-the-art in *ab-initio* simulations of the quantum-mechanical properties of crystalline materials.

Part One (Chapters 1–3) of the book provides a general introduction to the subject, addressed particularly to readers with a general knowledge in quantum chemistry, but not much confidence in solid state theory and its concepts.

Part Two (Chapters 4–7) is intended to give a deeper insight into the special algorithms and computational techniques which are currently adopted in *ab initio* computer codes for crystals.

Part Three (Chapters 8–10) presents in parallel three different programs which are available to all interested potential users on request, and based on very different approaches. These presentations may help newcomers in the field to understand the meaning hidden in the acronyms, and to choose the most suitable tool for their needs.

Finally, **Part Four (Chapters 11–16)** is an attempt to show what kind of information on the observable properties of condensed systems can be obtained from *ab initio* quantum-mechanical calculations. In particular, Resta's contribution demonstrates that important observables have become accessible to simulation, using quite unconventional new approaches. The last chapter, devoted to the hot topics of superconductivity, shows the importance of finding the connection between the results of *ab initio* calculations and high-quality theoretical schemes using parameterized Hamiltonians.

The publishing of these notes and their distribution to all the students of the above mentioned School has been possible thanks to the support of the Italian CNR (Consiglio Nazionale delle Ricerche).

A preliminary draft of these Proceedings has been distributed among attendants of the 1995 School organized under contract CHRX-CT93-0155 of the Human Capital & Mobility Programme of the European Community, which has provided additional funding for the work of revision.

I would finally like to thank Dr. Fiona Healy, who has read the manuscripts with patience and intelligence, and corrected their English, when necessary and when possible.

Cesare Pisani

Torino, May 1996

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