

ACCURATE ENERGETICS OF CONDENSED MATTER WITH QUANTUM CHEMISTRY

Organisers:

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Summary

The workshop was held at CECAM, Ecole Normale Supérieure, Lyon from Monday 26th May to Thursday 29th May 2008, as envisaged in our original proposal. The workshop began at 14:00 on the Monday and finished at 12:30 on the Thursday. In addition to the three organisers (Gillan, Shluger and Michaelides, all from University College London), there were 23 invited speakers and 24 other participants. Each of the 23 invited talks consisted of 30 minutes of presentation and 15 minutes of discussion. There were also 12 posters, which were presented in a poster session on the Tuesday evening.

As described in our original proposal, the purpose of the workshop was to review and discuss the efforts of the participating research groups to go beyond density functional theory by using wavefunction-based methods stemming from quantum chemistry theory to calculate the energetics of extended systems, focusing mainly on the bulk and surface of materials, but with some attention also given to biological molecules. We organised the invited talks into five themes: high accuracy for exchange and correlation (six talks); periodic Hartree-Fock and post-Hartree-Fock (five talks); incremental, hierarchical and Fragment-Molecular-Orbital methods (four talks); embedding and excited states (six talks); and surface science (two talks).

The workshop was highly successful, and all the talks generated lively discussion. It was clear from the workshop that wave-function-based quantum-chemistry methods are playing an increasingly important role, and that for some problems it is already possible to overcome the limitations of DFT for condensed matter systems. The organisers believe that the workshop will be seen in the future as a significant landmark in the continual evolution of computational condensed-matter science. Of the many important points that emerged from the workshop, we suggest the following as particularly noteworthy:

- It is becoming possible to apply high-level quantum chemistry methods to periodic systems, with increasingly good control over basis-set convergence;
- Quantum chemistry methods are increasingly being used to test and correct DFT predictions;
- There is a strong trend now to introduce quantum-chemistry techniques (e.g. second-order Møller-Plesset) into periodic codes (e.g. VASP, FHI-AIMS) that have up to now been based on DFT;
- Rapid progress is being made in embedding quantum-chemistry methods in more approximate techniques;
- Methods based on the incremental technique and on the loosely related Fragment Molecular Orbital scheme show great promise for the future.

- The power of quantum chemistry techniques for calculating the energies of electronic excited states is rapidly improving.

Scientific content and discussion

A major aim of the workshop was to bring together researchers whose backgrounds are in the condensed-matter physics and molecular quantum chemistry areas. The building of bridges between different communities is always important, but there are particularly strong reasons for attempting this now. A very important phase in the past history of density functional theory was the transfer of ideas and techniques from the physics community to the chemistry community. But now, we are seeing an equally important flow of ideas in the opposite direction, which we believe will be extremely fruitful for the future. We hope that our workshop will be seen to have played a useful role in this flow of ideas.

The major problem with density functional theory is that no way has yet been found of making its accuracy systematically improvable. The whole of contemporary wavefunction-based quantum chemistry, by contrast, is based on the idea of systematic hierarchies of correlation methods. The lowest level of correlation is usually taken to be 2nd-order Møller-Plesset, which already provides good accuracy for systems with large HOMO-LUMO gaps, including ionic (and perhaps partially ionic) materials and water. Importantly, MP2 accounts approximately for dispersion energy, which is completely absent from all the widely used forms of DFT. (Recent developments due to Lundqvist and Langreth and co-workers may be changing this situation.) The next step beyond MP2 is coupled-cluster methods, of which CCSD(T) is often regarded as the “gold standard” for many purposes. It is known that CCSD(T) gives an accurate description of dispersion for many systems. There are further steps in the coupled-cluster hierarchy such as CCSDT(Q), which will certainly be important in the future.

All this means that current efforts to apply MP2 and coupled-clusters methods to extended systems provide one of the most promising ways of going “beyond DFT”, and several of the talks at the workshop reported on these efforts. A number of different approaches are being followed. One important approach is to use so-called “local” MP2 techniques (talk by Schütz) within existing periodic Hartree-Fock codes, of which the CRYSTAL code is perhaps the most prominent. The talk by Pisani provided an update on development of the CRYSCOR code, which is based on this approach. Rather different from this is the implementation of the MP2 technique in plane-wave codes, for example VASP. The talk by Kresse reported on this, as well as presenting other ideas. Different again is the incremental approach, in which the spatial locality of correlation is exploited to develop a correlation hierarchy having linear-scaling properties. The remarkable success of this approach, using couple-cluster techniques for a wide variety of materials, including metals, was reported on in the talks by Friedrich and Paulus. Somewhat related is a hierarchical approach which has been successful in providing benchmark calculations of unprecedented accuracy on the perfect crystal, and which appears to be applicable to a variety of other materials (talk by Manby). Locality of correlation is also the basis for the Fragment Molecular Orbital method, which is now being applied by many groups (particularly in Japan) to large, complex biological systems (talk by Mochizuki). It is convenient to group here also the ambitious attempts to describe strongly correlated materials using quantum chemistry methods (Fulde). A strikingly original approach to the description of condensed matter using high-level correlation was reported by Alavi, who described a path-integral framework which allows infinite resummations leading to approximations closely related to MP2 and couple-cluster approximations. Practical calculations using this approach are now in progress on crystalline systems.

In addition to free-standing techniques that allow the direct computation of total energies using wavefunction based descriptions of correlation, a further important approach is the use of high-level quantum chemistry to correct density functional theory. A key concept here is that the difference between the total energies of clusters calculated using DFT and correlated quantum chemistry is expected to converge much more rapidly with respect to cluster size than the individual energies themselves. The fruitful use of this idea for the adsorption energies of organic molecules in zeolites was described by Sauer. The use of somewhat related ideas, in which MP2 clusters calculations are used to correct the deficiencies of DFT, was presented in the talk by Reuter.

In a somewhat different spirit from the foregoing approaches is the idea of embedding, in which molecular quantum chemistry methods are applied to a cluster of atoms, with the surrounding materials treated with one or more descriptions of lower accuracy. The embedding idea has a rather long history, but continues to be of great importance, as improved methods are developed for ensuring the smoothest possible joining of inner and outer regions. The overview talk by Kantorovich provided a description of general principles to guide embedding schemes, while the talk by Abarenkov dealt with a number of important technical problems in embedding schemes, including the troublesome problem of spurious surface states, and the question of reconstructing the orbitals of the infinite system from those of finite clusters. One of the important codes that has been used for embedding calculations over the past few years is the GUESS code, and the main developer of this code, Peter Sushko, gave a talk about current capabilities of this code. A different approach, in which high-level quantum chemistry methods are embedded in a DFT environment, was presented by Huang, who illustrated recently developed schemes using the examples of the CO molecule on Cu(111) and a magnetic Co atom on Cu surfaces.

There was a significant emphasis in the workshop on surface-science problems, because it is in this area that the weaknesses of DFT are often most apparent. Excellent examples of how quantum chemistry methods allow these weaknesses to be overcome were given in the talk by Jordan, who spoke about the paradigm problem of the buckling of the Si(001) surface, which has been a long-standing source of controversy, and interaction of water molecules with graphitic surfaces. This talk also reported recent work on the interaction of excess electrons with water.

An important area of research in which quantum chemistry methods have played a key role for many years is electronic excited states, where standard DFT is not normally useful. The talk by Klüner covered recent work from his group in which accurate ground and excited state potential energy surfaces are used in quantum dynamical wave-packet calculations. This approach allows direct comparisons with observable quantities, such as velocity distributions in photodesorption experiments. The talk by Seijo covered recent work of his group in using techniques from molecular quantum chemistry to calculate excited states of lanthanide and actinide ions in solids. It is also convenient to group here the talk by Hozoi, which described the use of wavefunction-based methods from traditional quantum chemistry to study the band structures of solids, including copper oxide high-temperature superconductors.

Although the main emphasis of the workshop was on wavefunction-based techniques for describing correlation, we wanted to include also some recent work on the use of hybrid DFT functionals in periodic calculations. A valuable overview of the merits of hybrid functionals for insulating systems, particularly in the calculations of vibrational frequencies, was given by Dovesi. Current efforts to improve these methods still further, using techniques based on range separation (i.e. separation of the spatial range over which exact exchange is used), were described by Scuseria. Exciting new developments in the use of hybrid functionals in ambitious molecular dynamics simulations were reported by VandeVondele. As an antidote to excessive optimism in the use of hybrid functionals, Pacchioni presented a valuable set of cautionary tales which made it

clear that complete faith in any single version of DFT, including hybrid functionals, remains unwise.

Future directions

It is highly encouraging for the future of condensed matter modelling that we were able to assemble such a distinguished set of speakers, who are taking such a wide variety of approaches to going “beyond DFT”. The meeting made it clear that, for some problems, practical calculations that are considerably more accurate and reliable than DFT are already feasible. It is clearly desirable that scientists who are primarily interested in applications should now start to take an interest in the new methodologies, and we feel confident that this will happen increasingly in the next few years.

Final programme

Monday 26th May

12:00 onwards: registration

Welcome by organisers

Session 1: High accuracy for exchange and correlation (I)

14:00 – 14:45 K. D. Jordan (University of Pittsburgh, USA)
“Case studies of systems with strong electron correlation effects”

14:45 – 15:30 K. Reuter (Fritz-Haber-Institut der MPG, Berlin, Germany)
“Towards an exact treatment of exchange and correlation in materials”

15:30 – 16:00 Coffee break

Session 2: Periodic Hartree-Fock and post-Hartree-Fock (I)

16:00 – 16:45 R. Dovesi (Università di Torino, Italy)
“Quantum mechanical simulation of the vibrational properties of crystalline solids, and interpretation of modes. The case of garnets and related minerals”

16:45 – 17:30 M. Schütz (Universität Regensburg, Germany)
“Local correlation methods for periodic systems”

Tuesday 27th May

Session 3: High accuracy for exchange and correlation (II)

09:00 – 09:45 G. Scuseria (Rice University, USA)
“Non-local exact exchange: range separation, hybridization and local variants”

09:45 – 10:30 A. Alavi (Cambridge University, UK)
“Electron correlation via path-counting: from molecules to metals”

10:30 – 11:00 Coffee break

Session 4: Incremental, hierarchical, Fragment Molecular Orbital (I)

11:00 – 11:45 B. Paulus (Freie Universität Berlin, Germany)
“Explicitly correlated ab initio methods for metals”

11:45 – 12:30 Y. Mochizuki (Rikkyo University, Japan)
“Recent progress in the Fragment Molecular Orbital method”

12:30 – 14:00 Lunch break

Session 5: High accuracy for exchange and correlation (III)

14:00 – 14:45 J. Sauer (Humboldt-Universität zu Berlin, Germany)
“Accurate energetics of transition structures and intermediates by hybrid MP2:DFT and DFT+Disp calculations”

14:45 – 15:30 P. Fulde (MPI für Physik komplexer Systeme, Germany)
“Strongly correlated electrons treated by quantum chemical methods”

15:30 – 16:00 Coffee break

Session 6: Embedding and excited states (I)

16:00 – 16:45 I. V. Abarenkov (St. Petersburg State University, Russia)
“On the embedding potential method in the condensed-matter electronic-structure theory”

16:45 – 17:30 P. Huang (Lawrence Livermore National Laboratory, USA)
“Embedded configuration interaction theory for solids: Application to strongly correlated adsorbates on metal surfaces”

17:30 – 19:00 Poster session

Wednesday 28th May

Session 7: Surface science

09:00 – 09:45 G. Pacchioni (Università di Milano-Bicocca, Italy)
“Electronic structure of insulating oxides and their surfaces: Are hybrid DFT functionals the right solution?”

09:45 – 10:30 T. Klüner (Universität Oldenburg, Germany)
“Accurate energetics of ground and excited states of molecules on surfaces”

10:30 – 11:00 Coffee break

Session 8: Incremental, hierarchical, Fragment Molecular Orbital (II)

11:00 – 11:45 J. Friedrich (Universität zu Köln, Germany)
“Using symmetry in the framework of the incremental scheme: Applications to molecular and periodic systems”

11:45 – 12:30 F. Manby (University of Bristol, UK)
“Cluster-based *ab initio* treatments of electron correlation in solids”

12:30 – 14:00 Lunch break

Session 9: Embedding and excited states (II)

14:00 – 14:45 L. Hozoi (MPI für Physik komplexer Systeme, Germany)
“Wavefunction based methods for excited states in solids: Correlation-induced corrections to the band structure of ionic oxides”

14:45 – 15:30 L. Kantorovich (King's College London, UK)
“Quantum-mechanical embedding based on system partitioning: some ideas”

15:30 – 16:00 Coffee break

Session 10: Periodic Hartree-Fock and post-Hartree-Fock (II)

16:00 – 16:45 G. Kresse (Universität Wien, Austria)
“Hartree Fock, MP2 and AC-FDT using the PAW method”

16:45 – 17:30 C. Pisani (Università di Torino, Italy)
“Ab initio post-HF estimates of vibrational frequencies in crystalline systems”

19:30 - Workshop dinner

Thursday 29th May

Session 11: Embedding and excited states (III)

09:00 – 09:45 L. Seijo (Universidad Autónoma de Madrid, Spain)
“Embedded cluster calculations on excited local states of lanthanide and actinide ions in solids”

09:45 – 10:30 P. Sushko (University College London, UK)
“An embedded cluster scheme for calculating defects and defect processes in wide-band-gap materials”

10:30 – 11:00 Coffee break

Session 12: Periodic Hartree-Fock and post-Hartree-Fock (III)

11:00 – 11:45 J. VandeVondele (Universität Zürich, Switzerland)
“Exact exchange for *ab initio* molecular dynamics in the Quickstep code”

11:45 – 12:30 Round-table discussion and concluding remarks