Psi-k workshop/summer school report

Quantum Monte Carlo in the Apuan Alps VII

and

Quantum Monte Carlo and the CASINO program VII

28th July - 12th August 2012,
Apuan Alps Centre for Physics, Vallico Sotto, Italy

M.D. Towler
University of Cambridge and University College, London

1 Summary

Every year since 2005 I have organized an international workshop *Quantum Monte Carlo in the Apuan Alps* and a summer school *Quantum Monte Carlo and the CASINO program* in my private institute - the 'Apuan Alps Centre for Physics' in the village of Vallico Sotto in Italy. The aim of the workshops is to bring together the greatest experts in the field (with associated students and young researchers) to discuss the development and application of the continuum quantum Monte Carlo (QMC) method in condensed matter physics and quantum chemistry. Those who have attended the workshops each year have indicated that they found them to be an intensely valuable experience - indeed, they have essentially been adopted by much of the international community as their 'Annual General Meeting'. Each year the workshop has been immediately followed by the summer school, the purpose of which is to provide students with a thorough working knowledge of the quantum Monte Carlo electronic structure method as currently used in quantum chemistry and condensed matter physics, and to show him or her how to use the Cambridge CASINO QMC program for serious scientific research. The course consists of around 20 hours of lectures by recognized experts in the field and a series of practical exercises in using the CASINO program led by its authors.

For summer 2012 we hosted a seventh workshop and school. The workshop was attended by 28 participants from 8 countries, and the school by 19 students from 12 countries. Both events were generally reckoned to be highly successful.

2 Description of the scientific content of and discussion at the event

QMC is a highly accurate method for calculating the electronic structure of atoms, molecules and materials whose computational cost - unlike most accurate quantum chemistry methods - scales reasonably with the system size (at best, as N^2). It has the further advantage that it can be made to scale linearly with the number of processors on a parallel machine, allowing the efficient utilization of the largest computational facilities available. In computational electronic structure theory it is vitally important to have a 'benchmark method' applicable to real systems where the results in individual cases can be relied upon, which is not really the case with the cheaper and more commonly used density functional theory (DFT) technique. This is particularly so in condensed-matter systems where most other

accurate quantum chemistry methods cannot be easily employed.

QMC deals directly with the full many-body Schrödinger wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Despite the additional complexity introduced by the dependence on $3N$ variables, we use this object because we know what equation to solve to get $\Psi(\mathbf{R})$ – the Schrödinger equation. In DFT the ground-state density depends only on three variables but the equation which it satisfies is, by contrast, completely unknown (efforts to find better approximations are vital and ongoing). As a consequence, QMC is capable of giving by far the more accurate energetics. There are two QMC techniques in widespread use – variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) – and there are a number of other more specialized variants. In VMC, we take the wave function as a given analytic form and use Monte Carlo numerical integration to evaluate the energy directly as the expectation value of the Hamiltonian: $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$. Monte Carlo integration is used as it is the only method that works for high-dimensional integrands (such as the many-body wave function). If necessary we change the shape of the wave function by varying the parameters which define it until the energy or the variance is minimized. In such calculations, Ψ is typically chosen to be the product of a Slater determinant of single-particle orbitals (e.g. from a DFT or Hartree-Fock calculation) multiplied by a *Jastrow factor* which is dependent on the inter-particle distances and allows efficient inclusion of both long- and short-range correlation effects (including van der Waals etc.). The Jastrow also imposes the exact cusp condition, that is, it introduces the correct divergence in the kinetic energy to compensate for the divergence in the potential energy as two electrons coalesce. Usually determinants from single-particle orbitals coming from DFT or Hartree-Fock calculations produce very accurate nodal surfaces.

The accuracy of VMC is ultimately limited by the analytic form chosen, which generally turns out not to have enough variational freedom to represent the true wave function. We thus turn to DMC, which is the ultra-accurate alternative used in most modern calculations. In DMC, Ψ is represented using a *non-analytic* method (the distribution in time and configuration space of an ensemble of diffusing particles). The algorithm encourages the particles to distribute themselves as in the true ground state through the use of a projection technique involving evolution in imaginary time. Once the particles have distributed themselves appropriately, we numerically integrate by sampling the wave function configuration space as before. In principle, this yields the exact ground-state energy.

The DMC technique exploits the similarity of the kinetic part of the Schrödinger equation to a diffusion equation, as in the theory of Brownian particles, while the potential part can be treated as a source or sink of the Brownian particles. With this equivalence, DMC simulates the diffusion, birth and death of these particle configurations or 'walkers', and the approximate Ψ from VMC is used to guide their diffusion, in a manner related to importance sampling. In practice, for many-body fermionic systems, convergence to the lowest energy *antisymmetric* state requires the use of the 'fixed-node approximation' and the method ceases to be exact. Nevertheless, we know from very many comparisons with experiment and quantum chemistry that fixed-node error is often extremely small, and we routinely test this in a variety of calculations. The only other significant approximation comes from the use of pseudopotentials, but again these errors can be estimated.

DMC has major advantages over other possible techniques for high-accuracy calculations: it is ideal for large parallel machines; with blip-function basis sets, convergence to the basis-set limit is rapid and automatic; scaling with system size is mild ($\sim N^3$ or less); and it can be used equally well for molecules in free space or for periodically repeated systems.

Despite such capabilities the technology of QMC is neither mature nor particularly widely used; its routine application to arbitrary finite and periodic systems, particularly those

containing heavier atoms, has long been just out of reach and there are still many open methodological and algorithmic problems to interest the computational electronic structure theorist. Many of these topics were widely discussed at the workshop.

Workshop

The following 28 participants attended the workshop:

Dario Alfè	UCL, London, U.K.
Sam Azadi	Imperial College, London, U.K.
Stefano Baroni	SISSA, Trieste, Italy
Benoît Braida	University of Paris, France
Dario Bressanini	Università dell'Insubria, Italy
Pascal Bugnion	University of Cambridge, U.K.
Dominik Domin	Université Paris-Est, France
Andrea Droghetti	Trinity College, Dublin, Ireland
Neil Drummond	Lancaster University, U.K.
Matthew Foulkes	Imperial College, London, U.K.
Mike Gillan	University College, London, U.K.
Kenta Hongo	JAIST, Japan
Martin Korth	University of Ulm, Germany
Pablo López Ríos	Cambridge University, U.K.
Ryo Maezono	JAIST, Japan
Mariapia Marchi	ESTECO S.p.A., Trieste, Italy
Alston Misquitta	Queen Mary University, U.K.
Bartomeu Monserrat-Sanchez	University of Cambridge, U.K.
Saverio Moroni	INFN, Trieste, Italy
Catherine Overy	Cambridge University, U.K.
Sebastiano Saccani	SISSA, Trieste, Italy
James Shepherd	Cambridge University, U.K.
Sandro Sorella	SISSA, Trieste, Italy
James Spencer	Imperial College, U.K.
Alex Thom	Imperial College, U.K.
Mike Towler	Cambridge University/UCL, U.K.
Lucas Wagner	University of Illinois, U.S.A.
Ching-Ming Wei	Academia Sinica, Taiwan

Richard Needs (UK), Cyrus Umrigar (USA), Mauro Causà (Italy) and John Trail (UK) were all booked in but were ultimately unable to attend.

In advance of the workshop I suggested that the following topics would be of particular interest:

(1) Further development of quantum Monte Carlo algorithms in terms of efficiency, speed, functionality, ease of use, scaling behaviour with system size, atomic number and number of processors.

(2) Application of the method to systems and situations where the less accurate density functional theory often fails, such as in strongly-correlated materials, metal-insulator transitions, magnetic properties and biological systems.

(3) The development of better many-electron wave functions and methods of optimization (particularly of parameters which change the nodal surface and thus have some potential to bypass the fermion sign problem).

(4) The calculation of QMC forces and their implementation in dynamical simulation meth-

ods.

(5) Pilot wave and quantum trajectory methods.

In the end, the participants gave 29 diverse presentations (listed in section 4) on a wide variety of topics, including much of the above.

Summer school

The following students attended the summer school:

Vikas Chauhan	Harish-Chandra Research Institute, India
Giorgio Cinacchi	University of Madrid, Spain
Fulvio Ciriaco	University of Bari, Italy
Simone Conti	University of Milano, Italy
Parag Deshpande	Northwestern University, U.S.A.
Li Ding	Chinese Academy of Sciences, China
Tomoyuki Hamada	University of Tokyo, Japan
Cui Hang	Chinese Academy of Sciences, China
Yingjin Ma	Nanjing University, China
Denis Magero	Chepkoilel University College, Kenya
Pawel Potasz	Politechnika Wroclawska, Poland
Ashish Radadiya	Saurashtra University, India
Abdulrafiu Tunde Raji	ICTP, Trieste, Italy
Anthony Reilly	Fritz-Haber-Institut, Berlin, Germany
Sahinur Reja	University of Cambridge, U.K.
Marc Segovia	University of the Republic, Uruguay
William Vigor	Imperial College, London, U.K.
Hui Wang	University of Saskatchewan, Canada
Chenyang Zhang	Nanjing University, China

Olga Castellano (Venezuela), Lalit Saini (India), Humberto Soscun (Venezuela), Jian Sun (UK), and Jonathan Lloyd-Williams (UK) all made last-minute cancellations largely due to insoluble bureaucratic problems.

Over the last few decades we in the Cambridge group have made a great effort to develop a general-purpose computer program - CASINO - and one of the main points of the school is to instruct the students in the use of this software. The code is capable of performing QMC calculations on a wide variety of systems, which may be of finite extent (atoms or molecules) or may obey periodic boundary conditions in one, two or three dimensions, modelling respectively polymers, slabs (or surfaces) and crystalline solids. Following recent modifications this software is ideally placed to exploit the so-called 'petascale computing' hardware with up to a million processors that is now becoming available. Systems containing thousands of atoms per molecule or per cell are thus now within reach of the QMC method using CASINO.

During the mornings, the students attended over 20 hours of lectures given by Drummond, López Ríos, and Towler. After lunch, they participated in extensive technical exercises involving the use of the CASINO code. Through these practical sessions they learnt (1) how to setup and compile the code on essentially any machine, (2) how to do variational Monte Carlo, diffusion Monte Carlo, and wave function optimization calculations, (3) how to generate trial wave functions from a variety of third-party codes, (4) various statistical analysis techniques, (5) how to work with pseudopotentials, and (5) how to deal with 'finite-size effects'.

On the final day, the students took a technical examination aimed at testing their newly-

aqcuired knowledge of quantum Monte Carlo. A prize was awarded for the highest mark, and this was ultimately achieved by Antony Reilly of the Berlin Fritz Haber Institute. This was followed by an 'advice session' where each student was asked to outline why he had attended the school and to explain his particular interest in quantum Monte Carlo stating what kinds of systems he wished to study. In most cases, the three lecturers were able to give detailed recommendations as to the best way to perform these calculations. Finally, an opportunity was also provided for students to give a short talk about their research.

3 Assessment of the results and impact of the event on the future direction of the field

Workshop

The vitality of research in this field was confirmed by the extremely wide variety of applications discussed, which included but was most definitely not limited to intermolecular interactions in water and ice, strongly-correlated materials, 'pancake bonding' in molecules, the 2D electron gas, electron-hole bilayers, high-pressure solid molecular hydrogen, the Hubbard model, water molecules and metal adatoms adsorbed on graphene, positronic molecules, applications in molecular spintronics including molecules such as $[Fe(H_2O)_6]^{2+}$ and $[Fe(NH_3)_6]^{2+}$, battery electrolyte solvents, soft-potential supersolids, two-dimensional ^{3}He, the 2D Heisenberg model, the earth's core, the binding energy of BN sheets, adsorbate-induced reconstruction on Si(111), the energetics of C, B, and Al clusters, phonon wave functions, base-pair stacking in DNA, and the first applications of QMC to molecular crystal systems (involving para-diiodobenzene). As the power of available computers and the sophistication of the algorithms and software increases, it is clear that the size and complexity of the systems that can be treated within QMC continues to rise rapidly. A number of researchers, including, Gillan, Wei, Maezono, and Alfè (who outlined his proposals for treating giant 'buckyball catcher' molecules with QMC) are particularly active in pushing the boundaries of what calculations can be done for real systems.

A number of more technical questions were addressed. These included the scaling of DMC calculations with processor number, with evidence presented that DMC can be made to scale essentially perfectly to well over 100,000 processor cores (that is, doubling the number of cores halves the required computer time). Two speakers looked at different approaches to adapting QMC codes to use the GPU accelerators that are both an increasingly important component of the most powerful supercomputers and also a potentially inexpensive way to to get high parallel performance from cheaper machines. This was evidently less successful, and it is clear that adapting existing complex codes for GPU use is difficult and that developments in both hardware and software (particularly including compilers) are required before this sort of thing becomes routine.

Efforts to use DMC techniques in molecular dynamics calculations were analyzed, as were finite size-effects in molecule-surface adsorption. Marchi outlined the work of her commercial company ESTECO, and gave an interesting analysis of complex optimization algorithms under development that could be of use in this field. López Ríos presented his work on his technical development of a new and entirely general form of Jastrow factor and his implementation of it in the CASINO program. Drummond showed how to use QMC to calculate Fermi-liquid parameters in the 2D electron gas. Bugnion explored the possibility of making better wave functions based on two-particle geminals.

A significant number of people in groups in London and Cambridge are involved with

stochastic Monte-Carlo approaches to classic quantum chemistry techniques such as CI and coupled cluster, and these efforts were the subject of a number of interesting talks by Foulkes, Spencer, Thom, and Shepherd. The FCI-QMC technique can reproduce the results of full CI calculations (for a given finite basis) essentially exactly but in considerably less time, and it is now possible to calculate energies for systems very much larger than was possible before. The stochastic coupled cluster technique discussed by Thom can reproduce large coupled cluster calculations much more quickly; it is considerably simpler to implement than deterministic coupled-cluster, and is feasible on workstations and very parallelizable. Foulkes talked about density-matrix QMC, an FCI-QMC technique that works in the space of operators/matrices instead of in the space of states and vectors. This makes finite temperature properties accessible and has considerable advantages in calculating expectation values for operators that do not commute with the Hamiltonian.

In my opinion, *Quantum Monte Carlo in the Apuan Alps* was a fascinating meeting showcasing the health and vigour of the field, and the talent and dynamism of many of the people working in it.

Summer school

The Vallico Sotto summer school programme has evolved over many years and is designed to address the problem of lack of experienced users of quantum Monte Carlo in general and of the CASINO program in particular. Over the years we have trained almost 200 people in the use of this important technique.

Comments received from almost all the participants after the school made it clear that on the whole the students greatly enjoyed the course and found it extremely beneficial. In particular they expressed the opinion that the course had the right balance between formal lectures, technical exercises, and social interaction (the students are strongly encouraged to take time to develop relationships which might form the basis of future collaborations).

On departure the students were provided with a copy of the CASINO code, and in the last couple of months I (MDT) have been in continuous email contact with a good proportion of the students who are now engaged in their first formal research projects in quantum Monte Carlo.

One negative aspect of the 2012 school was that the total number of students was markedly smaller than in previous years (only nineteen students made it to Vallico Sotto). This was partly due to a significant number of last-minute cancellations largely caused by evidently increased bureaucratic difficulties (e.g. visas being arbitrarily refused by Italian consulates). The number of European students was also markedly down (possibly due the current economic difficulties). Quantum Monte Carlo is clearly taking off in China and India, and we received a greatly increased number of applications from both countries. It was also noted that the gender balance was very poor, and for the first time no female students attended the school. In future years we will work to widen participation, and to return European contributions to former levels in line with that expected in accepting funding from the ESF.

4 Final programme of the workshop

The slides for almost all the talks presented have been made available on the Institute web site: `www.vallico.net/tti/qmcitaa_12`. In order of presentation, the talks given were:

Mike Gillan (`m.gillan at ucl.ac.uk`)
'*DFT troubles with water? QMC to the rescue!*'

Lucas Wagner (lkwagner at illinois.edu)
'*Correlations in strongly-correlated materials*'

Benoit Braida (braida at lct.jussieu.fr)
'*A valence bond / quantum Monte Carlo study of "pancake" bonding*'

Sandro Sorella (sorella at sissa.it)
'*Recent results on the Hubbard model by quantum Monte Carlo and petaflops supercomputers*'

Matthew Foulkes (wmc.foulkes at imperial.ac.uk)
'*Density matrix full-configuration interaction QMC*'

James Spencer (j.spencer at imperial.ac.uk)
'*The sign problem in FCIQMC and other short stories*'

Alex Thom (a.thom at imperial.ac.uk)
'*Stochastic coupled cluster theory*'

Dario Bressanini (dario.bressanini at uninsubria.it)
'*Fishing for positronic compounds*'

Mariapia Marchi (marchi at esteco.com)
(1) '*ESTECO*'
(2) '*Optimization tools beyond QMC*'

James Shepherd (js615 at cam.ac.uk)
'*A full configuration interaction (quantum Monte Carlo) perspective on the 3D homogeneous electron gas*'

Alston Misquitta (am592 at cam.ac.uk)
'*Finite-size effects in molecule-surface adsorption*'

Martin Korth (martin.korth at uni-ulm.de)
'*Computational high-throughput screening of advanced battery electrolyte solvents*'

Bartomeu Monserrat-Sanchez (bm418 at cam.ac.uk)
'*Phonon wave functions and electron-phonon interactions in semiconductors*'

Andrea Droghetti (drogheta at tcd.ie)
'*First principles studies of spin-crossover molecules*'

Ching-Ming Wei (cmw at phys.sinica.edu.tw)
'*Materials simulations using quantum Monte Carlo*'

Sebastiano Saccani (ssaccani at sissa.it)
'*Soft-potential supersolids*'

Saverio Moroni (saveriomoroni at gmail.com)
'*Two-dimensional 3He*'

Dominik Domin (domindominik at gmail.com)
'*Potential energy surfaces with quantum Monte Carlo*'

Mike Towler (mdt26 at cam.ac.uk)
'*Massively-parallel QMC calculations: CPUs, GPUs, and DMC molecular dynamics*'

Ryo Maezono (rmaezono at mac.com)
'*GPGPU acceleration of* CASINO *blip routine*'

Dario Alfe (d.alfe at ucl.ac.uk)
'*Thermal and electrical conductivity of the Earth's core*'

Neil Drummond (n.drummond at lancaster.ac.uk)
'*Quantum Monte Carlo calculations of the Fermi liquid parameters of the 2D homogeneous electron gas*'

Stefano Baroni (baroni at sissa.it)
'*Classical transition rates and quantum tunnelling splitting from path-integral Monte Carlo*'

Pablo Lopez Rios (pl275 at cam.ac.uk)
(1) '*Phase diagram of the symmetric electron-hole bilayer*'
(2) '*Framework for constructing generic Jastrow correlation factors*'

Sam Azadi (s.azadi at imperial.ac.uk)
'*Quantum Monte Carlo study of high-pressure solid molecular hydrogen*'

Pascal Bugnion (pob24 at cam.ac.uk)
'*The Geminal-Jastrow wave function in bulk materials*'

Kenta Hongo (kenta_hongo at mac.com)
'*A quantum Monte Carlo study of noncovalent interactions*'

5 Final programme of the summer school

The summer school featured the following lecture topics, in addition to practical afternoon exercises:

Mike Towler

- '*Quantum Monte Carlo : a practical solution to the correlation problem in electronic structure calculations*'

- '*The* CASINO *program : a basic introduction to functionality and input/output*'

- '*Three QMC scaling problems: many atoms, many protons, many processors*'

- '*Forces and dynamics. Expectation values other than the energy*'

- '*Practical issues when using pseudopotentials with* CASINO'

Neil Drummond (University of Lancaster, U.K.)

- '*Diffusion Monte Carlo*'

- '*Optimization of many-electron wave functions*'

- '*Ewald interactions and finite size errors*'

- '*Some recent applications of quantum Monte Carlo simulation*'

Pablo López Ríos (University of Cambridge. U.K.)

- '*Statistics in quantum Monte Carlo*'

- '*Wave functions beyond Slater-Jastrow for QMC*'

- '*Pseudopotentials for QMC*'

Exercises

- '*Distribution, setup and compilation of the* CASINO *program*'

- '*Basic use of the* CASINO *program - simple VMC, DMC calculations*'

- '*Wave function optimization with* CASINO'

- '*Trial wave function generation with other programs (*CRYSTAL/PWSCF/CASTEP *etc.)*'

- '*Advanced use of the* CASINO *program*'

- '*General* CASINO *applications*'

More informal details of both events, together with talk slides, photographs, and comments by participants can be found on the Institute web site.