promoting access to White Rose research papers

White Rose
Research Online

Universities of Leeds, Sheffield and York
http://eprints.whiterose.ac.uk/

Paper published in **Zeitschrift für Kristallographie.**

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/8521/

Published paper
Clark, S.J., Segall, M.D., Pickard, C.J., Hasnip, P.J., Probert, M.I.J., Refson, K. and Payne, M.C. (2005) *First principles methods using CASTEP.* Zeitschrift für Kristallographie, 220 . pp. 567-570.
http://dx.doi.org/10.1524/zkri.220.5.567.65075

White Rose Research Online
eprints@whiterose.ac.uk

Z. Kristallogr. **220** (2005) 567–570

© by Oldenbourg Wissenschaftsverlag, München

First principles methods using CASTEP

Stewart J. Clark*[,I], Matthew D. Segall[II], Chris J. Pickard[II], Phil J. Hasnip[III], Matt I. J. Probert[IV], Keith Refson[V] and Mike C. Payne[II]

[I] University of Durham, Department of Physics, Science Laboratories, South Road, Durham, DH1 3LE, UK
[II] University of Cambridge, Department of Physics, Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK
[III] University of Cambridge, Department of Materials Science and Metallurgy, Pembroke Street, Cambridge, CB2 3QZ, UK
[IV] University of York, Department of Physics, York, YO10 5DD, UK
[V] Rutherford Appleton Laboratories, Chilton, Didcot, Oxfordshire, OX11 0QX, UK

Received June 25, 2004; accepted October 21, 2004

CASTEP Computer program / Density functional theory / Pseudopotentials / ab initio study / Plane-wave method / Computational crystallography

Abstract. The CASTEP code for first principles electronic structure calculations will be described. A brief, nontechnical overview will be given and some of the features and capabilities highlighted. Some features which are unique to CASTEP will be described and near-future development plans outlined.

1. Introduction

The CASTEP programme [1, 2] is a first principles quantum mechanical code for performing electronic structure calculations. Within the density functional formalism it can be used to simulate a wide range of materials including crystalline solids, surfaces, molecules, liquids and amorphous materials; the properties of any material that can be thought of as an assembly of nuclei and electrons can be calculated with the only limitation being the finite speed and memory of the computers being used. This approach to simulation is extremely ambitious, given that the aim is to use no experimental (empirical) data, but to rely purely on quantum mechanics.

Before describing CASTEP in more detail, a brief history of the code follows. It was originally developed by Payne and co-workers in the late 1980's and early 1990's [2]. It quickly became a widely used code for electronic structure calculations. Subsequent developments and new technologies were added by a large and disparate number of collaborators and researchers. This mode of code development soon made further enhancements difficult to implement since there was no modular structure to the code and no written specification. This quickly became a hindrance to research, therefore from 1999, CASTEP has been completely redesigned from the ground up by the authors of this paper [4] and a new modular Fortran 90 code written. Due to the new code design, new methods and technologies are quickly and easily added to CASTEP, allowing users to rapidly take advantage of such developments. In addition, the new CASTEP code has been designed for parallel computers from the very beginning, allowing much larger problems to be tackled.

2. Background theory

While is not possible to solve the N-electron Schrödinger equation directly, density functional theory (DFT) [5, 6] gives us, in principle, a method to determine the ground state electronic structure of a system. A full review of its applicability to CASTEP can be found in references [1–3]. A brief summary of the methodology for electronic structure calculations as implemented in CASTEP is as follows: a set of one-electron Schrödinger (Kohn-Sham) equations are solved using the plane-wave pseudopotential approach [2]. The wavefunctions are expanded in a plane wave basis set defined by use of periodic boundary conditions and Bloch's Theorem. The electron-ion potential is described by means of *ab initio* pseudopotentials within both norm-conserving [7] and ultrasoft [8] formulations. Direct energy minimisation schemes are used to obtain, self-consistently, the electronic wavefunctions and corresponding charge density. In particular the conjugate gradient [2] and density mixing [9, 10] schemes are implemented. Also, the robust electron ensemble DFT [11] approach can be used for systems with partial occupancies (in particular, metals).

Although the total energy is the central quantity, the response of that energy to external influences is extremely important and can lead to further direct comparisons with experimental data through the calculation of experimental observables. If we perturb the system in some way then the total energy can be expanded as a perturbation series. There is a wide array of physical properties that then become accessible to us. For example, if a second order energy is calculated with respect to a given perturbation we can then obtain the following:

---

* Correspondence author (e-mail: s.j.clark@durham.ac.uk)

Perturbation		Physical quantity
Atomic positions	→	phonons
Electric field	→	dielectric properties
Magnetic field	→	NMR
Lattice parameters	→	elastic constants
k-point	→	Born charges

3. CASTEP capabilities

3.1 Background

CASTEP is a fully featured first principles code and as such its capabilities are numerous. Aiming to calculate any physical property of the system from first principles, the basic quantity is the total energy from which many other quantities are derived. For example the derivative of total energy with respect to atomic positions results in the forces and the derivative with respect to cell parameters gives stresses. These are then used to perform full geometry optimisations and possibly finite temperature molecular dynamics. Furthermore, symmetry and constraints (both internal and external to the cell) can be imposed in the calculations, either as defined by the user, or automatically using in-built symmetry detection.

3.2 Ease of use

CASTEP uses a *freeform* file format so that only the specific commands required for a given calculation need to be given. The values of all input variable have defaults set, with an intelligent selection of the essential parameters such as basis set size (plane wave cut off energy), *k*-point sets, Fourier transform grids and so on. Command line running of the code is simple with an output file summarising the calculation as it proceeds and a binary formatted file containing the details such as wavefunction coefficients and charge densities. In addition there is a command line help feature.

The code can be used in either serial or parallel. Running in parallel is straightforward; the number of nodes is specified on the command line and an intelligent default parallel strategy is chosen depending on the number of processors used and the number of *k*-points in the calculation.

A graphical user interface is available from Accelrys, Inc, namely the Materials Studio package which can be used to build the initial structure, generate input files, run the calculation, and finally analyse the data. It can be easily used to create charge density isosurfaces, to visualise band structures, to analyse phonon data and so on.

3.3 Summary of capabilities

The physical properties of materials that can be calculated using CASTEP include:

- *Total energies:* Calculation of total energy, forces, stresses, and elastic constants.
- *Electronic structure:* Electronic charge densities, orbitals, electrostatic potentials, band structure, total and partial electronic density of states, Mulliken population analysis, and optical properties (such as reflectivity, absorption, refractive index, dielectric function), subject to the usual DFT band gap considerations.
- *Geometry:* Optimisation of atomic positions and unit cell parameters, either constrained or unconstrained and under external pressure and stresses.
- *Molecular dynamics:* Finite temperature molecular dynamics can be performed under various conditions such as constant temperature, energy, volume, and pressure.
- *Transition states:* The LST/QST methods are used to find transitions states.
- *Phonons:* Using density functional perturbation theory (DFPT), phonon frequencies and eigenvectors are calculated which can be used to give the Gibbs free energy, entropy, enthalpy, Debye temperature, heat capacity, and a measurement of phase stability.
- *Electric field response:* DFPT is used to calculate the response of the system of an external electric field yielding bulk polarisabilities, dielectric constants, Born effective charges, LO/TO phonon splittings and the IR intensity of phonon modes.
- *Exchange and correlation:* The well known LDA and GGA functionals are included (such as the PW91, PBE and RPBE functionals), however non-local functionals such as the weighted density approximation (WDA), Hartree-Fock and exact/screened exchange are also available.

A list of publications using CASTEP can be found at www.accelrys.com/references/castep/.

4. Case studies

4.1 Improved molecular dynamics and geometry optimisation

The molecular dynamics implementation in CASTEP follows the Born-Oppenheimer approximation. The forces are calculated from the ground state electronic configuration at each MD step. Within this scheme the NVE, NVT, NPH, and NPT ensembles can be simulated. Temperature control is implemented via a chain of Nosé-Hoover thermostats or by performing Langevin dynamics in the appropriate phase space. Hydrostatic pressure is regulated by the use of either an Andersen-Hoover or Parrinello-Rahman barostat. Any combination of these schemes is allowable within the limits of the desired ensemble along with any combination of linear constraints. Other combinations of constraints are allowed, such as application of non-hydrostatic pressure and constraining or fixing lattice parameters.

Furthermore, CASTEP contains a new algorithm for optimising the configuration of a system of particles using damped molecular dynamics which has a much faster rate of convergence to the ground-state structure than other molecular dynamics based schemes [12]. It is possible to use this algorithm to select dynamically the optimum time step or to precondition the masses for modified dynamics, so as to produce additional significant efficiency gains especially as convergence is approached. Whilst this mini-

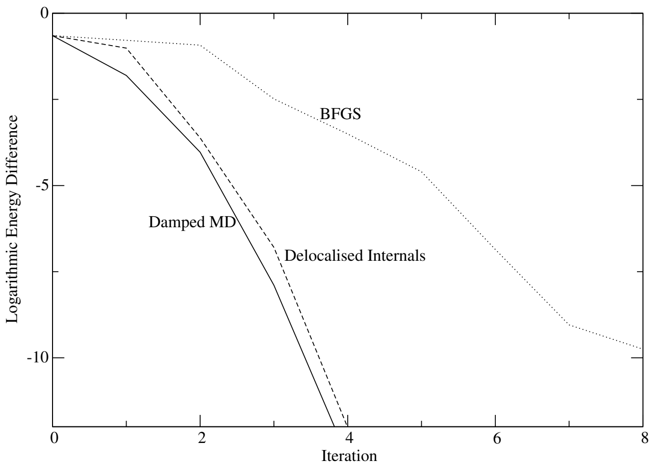

Fig. 1. The convergence of a geometry optimisation of a nitrogen molecule is shown using various geometry optimisation methods.

miser is a unique feature of CASTEP, the BFGS and delocalised internal coordinates methodologies are also implemented. An example if shown in Fig. 1 where the convergence of a geometry optimisation calculation is presented. In the plot, an "iteration" is defined such that the computational effort of each step is equivalent. Unfortunately such test cases are not general and the best choice of geometry optimisation scheme is often difficult to determine on a case by case basis. However, it has been found that damped MD of often best for molecular absorption on surfaces, while BFGS is best for crystalline materials. It is advised that small test cases be run using various optimisers as a guide before larger productions runs are attempted.

A number of mechanisms are used to improve performance, for example, wavefunction extrapolation techniques [13]. A significant speed up is obtained by not throwing away the Kohn-Sham wave-functions from the previous time-step. At the start of each new step, our self-consistent iteration process begins by minimising the electronic Hamiltonian due to the charge density at the previous time-step. If the motion of the atoms over a time-step is small, this will then require fewer subsequent SCF iterations to find the ground state than if we began from scratch. While this re-use of the wave-functions between time-steps does improve matters, we can go one step further and extrapolate the old Kohn-Sham wave-functions onto the new ionic positions at each time-step [14]. This gives us an even better starting point for the minimisation process and therefore requires fewer SCF cycles. An example is shown in Fig. 2 where the potential energy of a silicon crystal is plotted against CPU time in a molecular dynamics simulation with and without the use of wavefunction extrapolation.

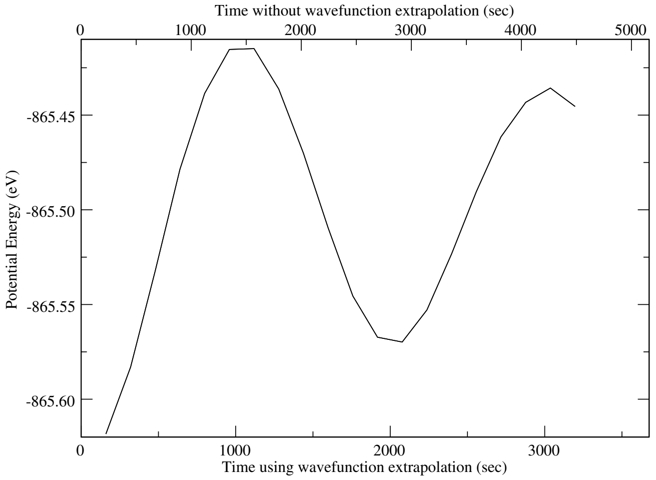

Fig. 2. The potential energy of a short molecular dynamics simulation of Si in the diamond structure is shown. The CPU time is compared for MD with and without wavefunction extrapolation.

4.2 NMR calculations

It has recently been shown how to calculate NMR chemical shifts in both molecules and solids within DFT and using pseudopotentials to describe the core-valence interactions [15]. The approach is based on gauge including projector augmented waves (GIPAWs), themselves derived from Blöchl's PAW electronic structure method and is now implemented in CASTEP. The calculated chemical shifts are typically good to about a percent of the measured shift range, which is not unusual for properties calculated using DFT. The GIPAW approach is a general method for the prediction of magnetic response properties, and it has also been applied to the prediction of electron paramagnetic resonance (EPR) g-tensors of defects in silica [16].

The first application of the GIPAW method was to elucidate the atomic structure of icosahedral boron carbide, where both X-ray and neutron techniques had failed to locate the carbon atoms in the B_4C structure [17].

In an another application, ^{17}O NMR parameters, both the chemical shifts and the quadrupolar coupling constants, were calculated for a variety of SiO_2 polymorphs [18]. The calculated NMR parameters of cristobalite, quartz, coesite and zeolite faujasite were found to be in excellent agreement with experimental data, demonstrating that DFT is able to reproduce, with high accuracy, the ^{17}O NMR parameters in SiO_2 systems. This precision, absent in previous cluster based studies, was used to assign the spectrum of the zeolite ferrierite [18].

4.3 Non-local exchange and correlation

Using CASTEP, calculations can be performed using exchange-correlation (XC) functionals that go beyond the standard (semi-)local approximations of the LDA and GGA. It has recently been shown that non-local functionals [19, 20] such as the weighted density approximation can be used to accurately calculate the structure of the XC holes in real materials which allows for a fuller understanding of their electronic properties from a fundamental viewpoint. Such an example is shown in Fig. 3 where the LDA and WDA XC holes are shown for a low density region of a "cosinusoidal crystal"; an idealised inhomogeneous electron gas where the external potential is cosinusoidal. The WDA hole accurately describes the delocalised nature of the XC hole while the LDA, incorrectly, gives a spherically symmetric XC hole.

Also implemented within CASTEP are the wavefunction based XC functionals, such as exact exchange, screened exchange and Hartree-Fock methods. Although

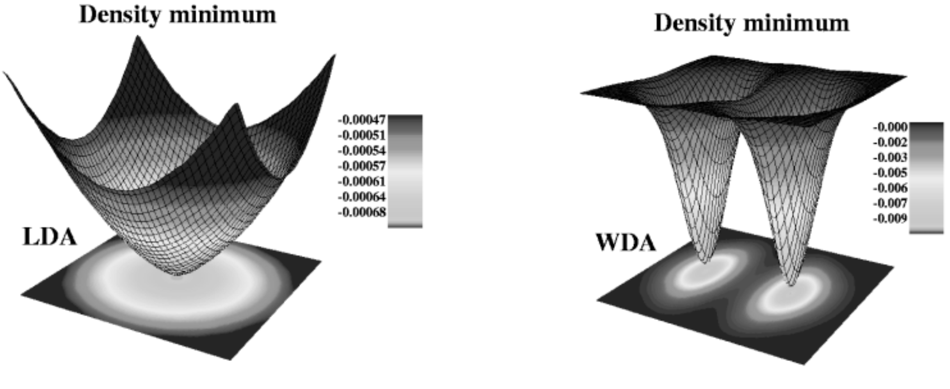

Fig. 3. The XC hole of a test electron (positioned at the centre of each plot) in a cosinusoidal crystal calculated using the LDA and WDA is shown in a region of low electron density.

these functionals require more computational effort than local functionals, they result in much improved electronic band gaps, in both solid and molecular systems. This leads to accurate optical properties such as reflectivity, absorption, and refractive index, without the need to introduce the empirical scissors operator to manually increase DFT band gaps.

5. Future development

Due to the modular design of the new CASTEP it is a reasonably easy task to implement new features in a quick and efficient manner. For example, nuclear quantum effects are being included using Feynman path integral MD. In addition, new XC functionals are constantly being developed, for example, to accurately describe van der Waals bonding [21]. DFPT methodologies are also being further developed and implemented to further increase the range of physical properties (and their accuracies) that can be predicted using CASTEP. Further developments include algorithmic improvements to decrease computer time and enhance efficiency in computer memory usage.

6. Availability

CASTEP can be obtained in several ways. Firstly, the UKCP consortium distributes a version of CASTEP to academic institutions within the UK (ukcp@dl.ac.uk and http://www.cse.clrc.ac.uk/cmg/NETWORKS/UKCP). Secondly, CASTEP is distributed commercially through Accelrys, Inc (http://www.accelrys.com) and is integrated into the Materials Studio package. Finally, CASTEP can be obtained in direct academic collaboration with the authors of the code.

References

[1] Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C.: First-principles simulation: ideas, illustrations and the CASTEP code. J. Phys. Cond. Matter. **14** (2002) 2717–2744.

[2] Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos J. D.: Iterative minimization techniques for abinitio total-energy calculations – molecular-dynamics and conjugate gradients. Rev. Mod. Phys. **64** (1992) 1045–1097.

[3] Milman, V.; Winkler, B.; White, J. A.; Pickard, C. J.; Payne, M. C.; Akhmatskaya, E. V.; Nobes, R. H.: Electronic structure, properties, and phase stability of inorganic crystals: A pseudopotential plane-wave study. Int. J. Quantum Chem. **77** (2000) 895–910.

[4] Dr P. Lindan of The University of Kent was also involved with the initial code specification.

[5] Hohenberg, P.; Kohn, W.: Inhomogeneous electron gas. Phys. Rev. **136** (1964) B864.

[6] Kohn, W; Sham, L. J.: Self-consistent equations including exchange and correlation effects. Phys. Rev. **140** (1965) A1133.

[7] Kleinman, L.; Bylander, D. M.: Efficacious form for model pseudopotentials. Phys. Rev. Lett. **48** (1982) 1425–1428.

[8] Vanderbilt, D: Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B**41** (1990), 7892–7895.

[9] Kresse, G.; Furthmuller, J.: Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B**54** (1996) 11169–11186.

[10] Alfe, D.: Ab initio molecular dynamics, a simple algorithm for charge extrapolation. Comp. Phys. Commun. **118** (1999) 31–33.

[11] Marzari, N.; Vanderbilt, D.; Payne, M. C.: Ensemble density-functional theory for ab initio molecular dynamics of metals and finite-temperature insulators. Phys. Rev. Lett. **79** (1997) 1337–1340.

[12] Probert, M. I. J.: Improved algorithm for geometry optimisation using damped molecular dynamics. J. Comput. Phys. **191** (2003) 130–146.

[13] Arias, T. A.; Payne, M. C.; Joannopolous, J. D.: ab initio molecular-dynamics techniques extended to large-length-scale systems. Phys. Rev. B**45** (1992) 1538–1549.

[14] Quiqley, D; Probert, M. I. J.: Langevin dynamics in constant pressure extended systems. J. Chem. Phys. **120** (2004) 11432–11441.

[15] Pickard, C. J.; Mauri, F.: All-electron magnetic response with pseudopotentials: NMR chemical shifts. Phys. Rev. B**63** (2001) 245101.

[16] Pickard, C. J.; Mauri, F.: First-principles theory of the EPR g tensor in solids: Defects in quartz. Phys. Rev. Lett. **88** (2002), 086403.

[17] Mauri, F.; Vast, N.; Pickard, C. J.: Atomic structure of icosahedral B4C boron carbide from a first principles analysis of NMR spectra. Phys. Rev. Lett. **87** (2001) 085506.

[18] Profeta, M.; Mauri, F; Pickard, C. J.: Accurate first principles prediction of O-17 NMR parameters in SiO_2: Assignment of the zeolite ferrierite spectrum. J. Am. Chem. Soc. **125** (2003) 541–548.

[19] Rushton, P. P.; Tozer, D. J.; Clark, S. J.: Description of exchange and correlation in the strongly inhomogeneous electron gas using a nonlocal density functional. Phys. Rev. B**65** (2002) 193106.

[20] Rushton, P. P.; Tozer, D. J.; Clark, S. J.: Nonlocal density-functional description of exchange and correlation in silicon. Phys. Rev. B**65** (2002) 235203.

[21] Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I.: Van der Waals density functional for general geometries. Phys. Rev. Lett. **92** (2004) 246401.