

## And the rest is chemistry...

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Using ab initio calculations to understand how surfaces relax, reconstruct and react chemically with water, ammonia or other molecules demands serious computer power. For oxides the task is especially difficult, and the work we are undertaking on  $\text{TiO}_2$  surfaces would be impossible without machines like the new CRAY T3D at Edinburgh. Using such massively parallel machines means that another exciting push forward for first-principles simulations is underway in the UK.

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In just ten years, quantum mechanical calculations of the energetics of condensed matter, based on the use of density-functional theory, pseudopotentials and a plane-wave basis set, have risen from relative obscurity to dominance in ab initio structural calculations [1]. Leaps in both algorithmic techniques and computer technology produced this explosive growth in the power of the method. In 1985 the key features which were to prove so successful were drawn together by Car and Parrinello [2]: the most important of these was that finding the self-consistent electronic ground state could be tackled through global minimisation rather than matrix diagonalisation. The crucial feature of this “Car-Parrinello” approach is the improved scaling with system size, meaning simply that more atoms can be studied for the same computer cost. However, for moderate system sizes (e.g. 20-100 silicon atoms) on conventional supercomputers this cost is still considerable, while for large systems it becomes prohibitive.

Naturally, then, there exists a strong desire to exploit the enormous potential of parallel computing technology which has been rapidly maturing over the same period. The focus of efforts within the UK has been the “Grand Challenge” project devoted to ab initio simulation on parallel computers, conceived to exploit the newest and best high-performance computer technology to do great science. The UK Car-Parrinello (UKCP) consortium of which our work is a part is a bigger and more ambitious outgrowth of the original project. Judged by any standards these efforts have been and continue to be remarkably successful scientifically, largely because they bring exceptional computer resources to bear on otherwise intractable problems,

The 320-processor, 64 MB-per-node CRAY T3D is comfortably the most powerful machine currently available to the UK’s academics, even though the theoretical 40 GFlop rating has not been approached in practice. The UKCP community is already exploring the capabilities of the new machine, benefiting from the several years of intensive code development and experience with parallel calculations using the CETEP [3] code. The reality is that calculations which were at the

limit of previous resources' capabilities are almost routine on the T3D, indicating that new horizons are within reach.

We believe that understanding chemical processes at the surfaces of oxide materials via first-principles simulation lies within these new horizons. Our project, funded by CRAY research and jointly managed by CCP3 and CCP5 at Daresbury, targets molecular processes at  $\text{TiO}_2$  surfaces. To place this in a broader context, three other  $\text{TiO}_2$  ventures are underway at Daresbury: one is using fluid dynamics to model gas-phase production of the material, funded by Tioxide Ltd.; a ROPA award from the OST is supporting classical modelling of the morphology and growth of  $\text{TiO}_2$  crystals; and a Europe-wide HCM collaboration applying crystal Hartree-Fock methods to oxides incorporates work on  $\text{TiO}_2$  surface properties. A clue as to why so much interest is being aroused comes from the diverse uses of  $\text{TiO}_2$ , which include those as a catalyst, a paint pigment and a gas sensor, all of which depend crucially on its surface chemistry. The amount of hard information to hand is surprisingly limited though, since experiments must overcome problems inherent in the study of oxides. To take an example, STM imaging runs into trouble due to surface charging. However, as previous first-principles work has shown [4], a vital, fundamental contribution to understanding can be gained from simulation. Add to these facts the nature of  $\text{TiO}_2$  - semi-ionic in character, with anomalously large, anisotropic dielectric constants and unusual vibrational properties - and a pleasant cocktail of incentive, challenge and possible reward is formed.

Our initial goal is to unravel the question of whether or not some of the surface orientations of  $\text{TiO}_2$  are more stable in a reconstructed state. An illustration of this appears in "HPC-Profile". While careful experimental work has shown that such reconstructions may occur [5], atomic-level interpretation of the results is difficult and sample condition hard to control. For us, even this relatively modest aim will involve dealing with a large system, and additionally the combination of transition-metal and oxygen ions results (through the difficult pseudopotentials) in very demanding calculations - a characteristic of Car-Parrinello studies of oxides [4]. Once we move onto more complex studies such as water absorption and dissociation, or the reaction of  $\text{SO}_2$  at  $\text{TiO}_2$  surfaces, the technical demands become enormous. It is no exaggeration to say that the T3D is at present the only resource for the job, and it offers an opportunity for this project, and others like it, to impact decisively upon problems at the very forefront of surface science research.

## References

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- [2] R. Car and M. Parrinello, "Unified approach to molecular dynamics and density-functional theory", *Phys. Rev. Lett.* **55**, 22 (1985)

- [3] The original density-functional plane-wave code CASTEP was written by Mike Payne in Cambridge. Subsequent parallelisation by Lyndon Clarke in Edinburgh produced CETEP, and many improvements and enhancements to both codes came from Payne, Ivan Stich, Victor Milman and others in the UKCP community. After more development of CETEP by Janusz Holender and Mike Gillan at Keele, the latest version of the code will be supported by Jim White, based in Cambridge.
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