

CCP1/CCP5 WORKSHOP
'Modelling of Localised States in Condensed Matter'
Keele University, 14th - 16th June 1995

In many different condensed-matter problems, one is interested in the properties of a highly localised group of atoms occupying a region perhaps less than 10 Å across, but which is strongly influenced by the surrounding medium. Examples include defects and impurities in crystals, molecules interacting with solid surfaces, and chemically reacting molecules in solution. The most effective strategy for tackling such problems theoretically should be to use an accurate quantum treatment for the small number of atoms of direct interest, and a simpler phenomenological treatment of the environment. However, the problem of matching the two very different kinds of treatment is highly non-trivial, and raises fundamental questions. This is the celebrated 'embedding problem'.

The three-day workshop, jointly supported by CCP1 and CCP5, brought together experts from a number of different fields, with the aim of comparing and analysing approaches to the embedding problem, and discussing ways of overcoming the difficulties that still exist. The following pages reproduce the workshop programme and the abstracts of the invited talks and the posters.

The organisers deliberately set out to invite participants from different backgrounds and with different research interests, and this led to extremely lively exchanges of views during the meeting. The participation of computational solid-state physicists, materials chemists and biochemists gave an almost unique opportunity to compare quantum chemistry methods based on the Hartree-Fock approach and solid-state methods based on density-functional theory, as well as semi-empirical and model-based methods, in the context of the embedding problem.

The meeting was generally agreed to have been highly successful. An obvious success was the setting up of entirely new contacts between research groups, which in some cases had been unaware of each other's existence. The opportunity to gain new perspectives on familiar problems from the vantage point of researchers in different fields was also invaluable. The meeting was also a chance to thrash out technical problems both in the formal discussion periods and outside the meeting. The organisers thank CCP1 and CCP5 for the financial support that made the workshop possible.

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Combined density functional and configuration interaction method for the electronic structure of solids with impurities

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The case of the open shells impurity atoms or molecules is considered.

The importance of correlation effects is discussed, and the relevant computational methods are briefly reviewed with examples from atoms and small molecules calculations.

The Local Density Approximation (LDA) can not be immediately applied for this case, as the wave function mixing several or many determinants is essential. The Many-Configuration Self-Consistent-Field (MC-SCF) method appropriate for the open shells atoms cannot be applied to a solid as it stands because the computing time scales very badly with the system size. The hybrid embedding scheme is proposed to incorporate the MC-SCF method for the impurity within solid state calculations done with LDA.

The idea is to introduce the intermediate region - a buffer (B) between the impurity (I) and the rest of the solid (S). The buffer should contain a comparatively small number of atoms so that MC-SCF calculation of the I+B can be practical. At the same time the one determinant wave function should make a good approximation to the buffer to enable the LDA calculations of B+S. The influence of S onto I+B is simulated with the embedding potential to be found from B+S calculations.

A simple model system was considered consisting of four pseudo-atoms, two one-electron pseudo-atoms representing I, one two-electron pseudo-atom representing B, and another two-electron pseudo-atom representing S. This system was calculated with LDA, HF, and MC-SCF methods. The local embedding potential was constructed and the proposed method was tested in comparison with the isolated I+B cluster approximation.

A hybrid shell-model/quantum mechanical treatment of defects in ionic crystals

A.H. HARKER

The ICECAP computer code adopts a mixed model for defects in ionic crystals, in which a quantum mechanical core region is embedded in a semi-classical shell model of the surrounding crystal. This talk will discuss the reasons for the choice of this hybrid model, and describe the way in which the interface between the quantum mechanical and semi-classical models is implemented in the code.

Some results will be presented which demonstrate the internal consistency of the model, and examples will be given of the application of the model to a variety of defect systems and processes.

The EMBED project: recent results, problems and prospects

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The EMBED project is being carried on for about eight years now by the Group of Theoretical Chemistry in Torino with several collaborations (Kantorovich, Catlow, Saunders, Sulimov, Allouche, Hess, Birkenheuer). Its aim is to produce efficient ab-initio computational techniques for the study of local electronic structures associated with point defects in otherwise perfect crystals. It is characterized by both the development of theories (based on the so-called perturbed-cluster (PC) approximation) and their implementation in a general-purpose computer program, whose first public version (EMBED93) has recently appeared [Pisani, Corà, Nada and Orlando, *Comp. Phys. Comm.* 82, 139 (1994)]. Because of this connection, the machinery employed for solving the fundamental equations is largely determined by the method adopted for determining the host crystal wavefunction. Our choice has been to refer to the Hartree-Fock LCAO technique as implemented in the CRYSTAL92 program [Dovesi, Saunders and Roetti, University of Torino and DRAL (1992)]. This communication illustrates the state of the project, its problems and prospects. Some recent results obtained with the use of the EMBED93 program (hydrogen adsorption and solution in lithium, ammonia protonation in zeolites, structural and chemical defects in ordinary ice) confirm that the approximation underlying the PC theory is well justified in many important cases, and that the code can provide useful results with acceptable computer requirements. On the other hand, the need for important improvements in both theory and algorithms has become evident. There are essentially two types of problems. Firstly, how to introduce simple corrections for taking into account changes induced by the defect in the 'external space' (flow of charge to or

from the defect region, polarization of the medium, long-range atomic relaxation, etc.) which are disregarded in the basic PC theory. Secondly, how to make the code more efficient (reasonable initial guesses to accelerate convergence of the SCF process, and the use of pseudopotentials for heavy atoms) and more powerful (estimate the correlation correction to the defect formation energy, and the possibility to study open-shell and multi-determinantal configurations in the cluster, corresponding both to the defect ground state and to local excitations). Work is in progress on some of these points, and the solutions proposed are briefly discussed.

Unrestricted Hartree Fock Method for local defects in crystals and at their surfaces

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In recent years the EMBED program has become a powerful tool for studying localised defects in crystals and adsorbates on well-ordered periodic surfaces. It is based on the Hartree-Fock method to determine the electronic structure of the defect systems under study. Up to now only the restricted Hartree-Fock technique has been implemented. Many important defects like core holes, open shell adsorbates and the description of bond breaking processes undergoing in the proximity of catalytic active surfaces, however, require an open-shell treatment. In the present communication the perturbed cluster equations underlying the EMBED program are presented and their extension for an unrestricted or restricted open-shell Hartree-Fock description of the electronic structure near the defect is discussed. The technique adopted to calculate the defect formation energy without subtracting two in principle infinite quantities and the impact of the open-shell method are presented too. To arrive at a self-consistent open-shell solution of the perturbed cluster equations during the SCF procedure several techniques have been introduced to properly initialise and control the parts of the density matrices recalculated in each SCF cycle. Preliminary results on typical open-shell defect systems are presented to demonstrate the range of applications which are now available with the new UHF option of the EMBED program.

The Relation Between Embedding and Linear Scaling

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In the last five years, there has been rapid progress in developing linear-scaling techniques for electronic-structure calculations - techniques in which the computer effort increases only linearly with the number of atoms. Many of these techniques are based either explicitly or implicitly on the approximation that the density matrix vanishes when the separation of its spatial arguments exceeds a chosen cut-off. But the embedding problem, if formulated in terms of the density matrix, also leads to the requirement that the latter be localized. This relation between embedding and linear scaling strongly suggests that recent linear-scaling ideas will be helpful for the embedding problem. The talk will outline an ab initio linear-scaling technique due to the present authors, and will suggest how it could be applied to the embedding problem.

New Tight-Binding Method (Molecule as Defect of Hilbert Space)

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The main idea of the method consists in the ‘embedding’ of the finite basis set of localized functions into the space spanned on the plane waves basis (Free-Electron Continuum); the potential \hat{V} is assumed to have nonzero matrix elements only over that set. The problem is quite similar to one of the ‘embedding’ of a defect region into crystal but the fact that as a rule only the part of the spectrum below the level of vacuum will be of interest to us simplifies our following reasoning. Resonance states can be also described in this method as against the standard quantum chemical procedure.

In the new method a finite set of basis orbitals $\{N\}$ is chosen and eigenvalues ϵ and eigenvectors $|N\rangle$ are found from the standard one-particle Hamiltonian H projected on to this basis set

$$\hat{H}_N = \hat{P}_N \hat{H} \hat{P}_N = \hat{T}_N + \hat{V}_N \quad (1)$$

where \hat{V}_N is the self-consistent potential including coulomb and exchange interactions and \hat{P}_N is the orthogonal projector on to the subspace $\{N\}$. Inclusion of continuum states can be now realized by transforming from \hat{H}_N in eq.(1) to the Hamiltonian \hat{H}_1 ,

$$\hat{H}_1 = \hat{T} + \hat{V}_N \quad (2)$$

If the one-particle spectrum of the Hamiltonian \hat{H}_N is found by application of the Rayleigh-Ritz variational method then the spectrum of \hat{H}_N can be obtained by the degenerate perturbation

technique of Lifshits or (equivalently) from the Kohn-Rostoker variational principle $\delta\Lambda = 0$ for the functional

$$\Lambda = \langle \psi_N | \hat{V}_N - \hat{V}_N \hat{G}_N^0 \hat{V}_N | \psi_N \rangle \quad (3)$$

where \hat{G}_N^0 is the projection of the free-electron Green function (or resolvent) for the kinetic energy operator $G^0 = (\epsilon - T)^{-1}$. This GF method is analogous to the embedding problem which occurs in the discussion of crystal defects in solid state physics but here the whole Hilbert space plays the role of the host crystal.

A complete exposition of the method, including mathematical details and computational peculiarities, such as the solution of the nonlinear eigenvalue problem and the estimation of Green-function matrix elements over Gaussian functions is given in ref.[1].

In ref.[2] we propose to estimate the total energy of a system in the new (Green-function) method as

$$E_{GF} = E_{HF} + 2 \sum_i (\epsilon_i^{GF} - \epsilon_i^{HF}) \quad (4)$$

where the summation is carried out over valence states. It seems that this supposition is reasonable for comparatively good bases, when ‘charge’ inside the given basis set $Q_N = Tr\rho_N$ converges to the number of electrons. It is possible that similar formulae will be true for methods which take into account electron correlation because the correction (4) concerns only the one-particle kinetic energy operator and does not involve the potential, which can be included in the correlation correction too.

Analysis of different ground state results of atoms and simple molecules allows us to formulate a semi-empirical correction to the one-particle energies

$$\epsilon = \frac{(2\epsilon_{GF} + \epsilon_{HF})}{3} \quad (5)$$

Using this correction improves the accuracy of the energy estimate by an order of magnitude. It seems that the correction must have a theoretical foundation which is so far not clear. A similar correction for the total energy can be proposed by the combination of eq.(4) and (5).

The GF method is more suitable than the HF one for the description of intermolecular interactions (see ref.3), including hydrogen bonding, because it gives the correct asymptotic behaviour of the tail of a wave function in the intermolecular space. In this space, where the potential is varying slowly, a corrected wave function will really be

$$\psi \sim \int G_N^0(\epsilon, \vec{r} - \vec{r}') \psi_N(\vec{r}') d\vec{r}'$$

where ψ_N is the HF wave function from the basis $\{N\}$. If $r \gg r'$ (ψ_N is localized at the origin of one of the molecules) then the asymptotic behaviour of ψ coincides with that of G^0 which corresponds to the correct quantum mechanical value

$$\frac{\exp(-\sqrt{-2\epsilon}r)}{r}$$

Thus the GF basis set obtained is corrected in the appropriate direction and we have to expect essentially a decrease in the basis-set superposition error which arises because the dimer basis set is larger than that of each monomer and this produces an artificial lowering of the dimer energy relative to that of the separated monomers.

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Embedding Calculations based on Ab Initio Pseudopotential Techniques

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Plane-wave, pseudopotential methods, based on density functional theory, have become established as one of the most important techniques for the first principles simulation of condensed matter. Embedding methods have the potential to considerably extend the scope of current pseudopotential calculations. To illustrate this I will focus on one particular problem, the recovery of information about core states and true, as opposed to pseudo, valence wavefunctions from a pseudopotential calculation. The motivation is that an ab initio simulation of the core will enable us to calculate the fully relaxed crystal charge density (which can be compared with accurate structure factor determination by X-ray and electron diffraction) and to calculate properties which depend on the density near the nucleus, such as hyperfine interactions in magnetic systems.

The basic idea is to construct an embedding potential, using Green's function matching techniques, on a sphere around an atom which then acts as a boundary condition in a fully self-consistent atomic calculation inside the sphere. The main technical problem is the accurate calculation of the Green's function on the embedding sphere from a plane-wave representation. A number of difficulties will be discussed, including completeness of the spectral representation and the need for accurate Brillouin zone integration. Results will be presented for the embedding potential and core reconstruction for the test case of bulk fcc Al.

The construction of accurate Green's functions from a plane-wave, pseudopotential calculation have many other applications and a number of these will be discussed, in particular in the context

of surface embedding problems.

A combination of the Quantum-Mechanical Perturbed-Cluster and the Semiclassical Mott-Littleton techniques for the study of charged defects in crystals.

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This talk focuses on defects that introduce long-range perturbations in the host crystal. Reference is made to the Perturbed-Cluster (PC) theory, presented earlier in this workshop by Prof. Pisani. The defect system is partitioned in a local zone, C, and an outer zone, D. In the standard PC theory both regions are treated quantum-mechanically (QM), with the approximation that the perfect crystal solution is used in zone D. The effects introduced by this approximation are now examined, and different levels of theory are proposed to overcome the limitations. In the case of charged defects, the long-range polarisation induced in the surrounding medium can be evaluated and included in the embedding procedure by means of a semiclassical (SC) treatment. This is based on the shell-model and on the Mott-Littleton theory. A new program, EMBRION, is being implemented, that includes this feature. In the new technique, at each cycle of the SCF procedure the polarising potential, V_q , created by the defect is computed with the QM method. The SC technique is used to describe how the ions in zone D polarise and displace under the effect of V_q , and how the field generated by zone D changes with respect to perfect crystal. This information is in turn used to correct the local QM Hamiltonian. The energetic contribution arising from the polarisation of the outer medium is also computed within the SC treatment. In the method proposed, the SC description of the outer zone is coupled to, and does not replace the QM. The requirements to make the two descriptions consistent are analysed.

Green function methods for surface state scattering studies and related problems

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As experimental surface science undergoes a transition from analysis to synthesis, theoreticians are posed new and challenging problems. Highlighting this are recent experiments which have demonstrated the controlled formation of surface structures, built atom-by-atom with the STM. Typical structures are comprised of c. 100 atoms, and cover an area of c. 1000 atoms. This is well beyond the capabilities of conventional electronic structure methods.

A particular feature of the experimental studies has been the observation of lateral standing electron waves on various surfaces of the noble metals, arising from the scattering by adatoms of electrons in Shockley surface states. Studies of this phenomena could offer insight into the two-dimensional electron gas, many-body effects at surfaces, electron localisation, and other fundamental and practical issues.

I will discuss recent progress on the development of theoretical methods for these problem. These include approaches based upon embedding techniques as well as multiple-scattering Green function calculations. The advantages and disadvantages of these approaches will be discussed, both in terms of ease of calculations, such as accommodating the large length-scale fixed by the surface state wavelength, and interpretive facility. Both approaches will be illustrated with recent results.

Simplified Electron Energetics in Car-Parrinello MD.

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In order to circumvent the computational cost of a full *ab-initio* description of the electronic structure in large-scale applications of Car-Parrinello MD, we have developed simplified representations of the electronic structure in the C-P scheme which are applicable to particular physical systems. These schemes could provide suitable embedding *environments* for more general quantum calculations since they are derived from the same well-specified electronic energy functionals which are used in the full quantum calculations.

For metals we use an LDA formalism which involves the use of the electron *density* as the basic variable and avoids the introduction of orbitals [*J. Phys. Condens. Matt.*, **5**, 3221 (1993)]. The form of the kinetic energy functional is chosen to incorporate several exact limits (uniform system, linear response and rapidly varying density) while the rest of the energy functional is exactly the same as in a Kohn-Sham calculation within the local density approximation. For metals the orbital-

free scheme has particular advantages – the dynamics are stable and Brillouin-zone sampling is avoided. The electronic part of the algorithm scales linearly with system size and large simulation cells and long run times become possible. Good results for simple metals have been obtained.

For ionic systems, the many-body aspects of polarization and dispersion interactions are included by adding additional degrees of freedom, which represent distortions of the electronic structure of an ion due to interionic interactions, to the ionic coordinates and extending the equations of motion accordingly [*J. Phys. Condens. Matt.*, **5**, 2687, (1993)]. Short-range corrections to the asymptotic induction and dispersion terms are parameterized on the basis of *ab-initio* electronic structure calculations. The polarizable ion model reproduces distinctive features of short- and intermediate-range order in MCl_2 melts (where M is a group IIA or IIB metal) and gives global energy minimum structures in agreement with experiment for the MX_2 crystals. Non-additive dispersion effects become important for systems with highly polarizable anions and influence the structure of systems such as CsAu markedly.

Quantum Mechanical Embedding Methods to Study Solvation

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Models of solvent-solute interactions in which the solute is described using quantum mechanical methods, and the aqueous solvent is described using either a continuum model or explicit water molecules, are described. Their use is illustrated by studies of molecular shape, solvation energies and molecular reactivity.

Ab initio model potential (AIMP) embedded-cluster studies of localised ground and excited states in ionic crystals.

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The *ab initio* model potential method (AIMP) is presented as a useful embedding technique based in the Group-Function Theory proposed and developed by McWeeny and Huzinaga. The method

is shown to be readily applicable to the calculation of the equilibrium geometry and electronic structure of localised ground and excited states in doped ionic crystals. Results of recent AIMP embedded-cluster calculations are presented which include (a) local structure properties and (b) electronic transitions (ground state absorptions, excited state absorptions, and fluorescence) in first-series transition metal doped oxide and fluoride crystals. The AIMP quantum embedding is shown to enable the calculation of the electronic structure of excited states with comparable accuracy to that attainable in the gas phase. This conclusion is illustrated along the AIMP study of mechanisms that compete with the laser activity in a family of tunable solid state laser materials.

Locality in the modelization and analysis of ionic materials

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The term locality is here interpreted to mean two rather different perspectives. On the one hand, localization of electrons in the orbital space is at the core of the Theory of Electronic Separability (TES). A hierarchy of models based on TES have been used to compute the geometry, vibrational and electronic spectra of Cu^+ centers in alkali halides, and the most relevant results will be reviewed.

On the other hand, Bader's *Atoms in Molecules* theory produces a detailed picture of the electronic distribution in the real space. Basic concepts such as the size, charge, energy and shape of an atom within a molecule or crystal come directly upon the wavefunction of the system. Recent application of this theory to ionic crystals is here presented and discussed.

Quantum cluster in polarisable crystal environment. Consistent microscopical approach

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During the last thirty years the molecular cluster model has been used quite extensively to study various point defects in a vast number of solids. At the same time, the complete understanding

of approximations underlying this model are still lacking, and therefore most of the methods implemented so far are based on intuitive models. The talk will focus on the Embedded Molecular Cluster (EMC) method based on the Theory of Electronic Separability and the Arrow Diagram technique. These allow one to account for the overlap of the wave functions associated with different structure elements, namely the molecular cluster and the structure elements of the perfect crystal which are around it. We will demonstrate how a consistent quantum-mechanical approach developed in the EMC method confirms a model of ‘*a quantum cluster in the semi-classical environment*’ currently used in a number of *ab initio* and semi-empirical computer codes. Since the interaction of the cluster with the outside region and that within it are considered similarly, the short-range potential imposed on the cluster because of the perturbed outside region appears to be consistent with the way in which atoms in the outside region interact with each other. The problem of calculating the polarisation in the outside region will also be addressed and discussed.

Thermal effects on the localized solutions of the Fröhlich/Holstein/Davydov Hamiltonian.

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The Fröhlich/Holstein/Davydov model describes the motion of a quantum quasiparticle in a lattice which interacts with the quasiparticle. Because of the quasiparticle/lattice interaction, localised states can form at $T=0K$. As temperature increases, however, the localized states become less stable. Important questions are the temperature at which the localized states become unstable and their lifetime in the unstable regime. While it is possible to answer the first question, the determination of the lifetime of localized solutions is still unresolved. A short review of this field, together with a discussion of the unsolved points and its possible relevance to biological processes, will be presented.

Self-consistent equations and gauge transformations of electron group functions

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Basic statements of the *Electron Group Functions* (EGF) method (known also as the *Theory of Electronic Separability*) are analysed, and general equations of the method are obtained.

The requirements of variational freedom of EGF's and their spatial separation are basic statements of the EGF method as they are necessary for taking into account the intragroup electron correlation while neglecting the intergroup one. But these requirements seem to be inconsistent with one another. This contradiction can be removed in certain cases using what we define here as the *Gauge Transformations* (GT) of EGFs. Particular examples are considered, one of them based on the notion of the *antisymmetrical annulment* of EGF [1]. The problem of existence of a general form of the GT is studied.

The total energy expression and self-consistent equations for arbitrary number of electron groups in the system with arbitrary numbers of electrons in the groups are written in the general form using an appropriate *Operator Technique* [2] and no approximation but the EGF one.

The transformation of the equations of the EGF method induced by some GT of EGFs is discussed. We also consider a possibility of applying GTs for constructing a pseudopotential produced by a correlated electron group as well as for localising EGFs.

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Localised states in transition metal insulators; an Hartree Fock description

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The Hartree-Fock theory of transition metal insulators provides a qualitatively correct description of the ground state. The delicate balance between localised and delocalised behaviour will be discussed. In recent studies the response of the ground state to doping of electrons and holes has been examined. We present results of these calculations and their relationship to various spectroscopic measurements.

Interaction of Methane with a Surface V-Centre on MgO(100): ab Initio Cluster Model Study

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To describe the interaction of methane with a cation vacancy site in the (100) surface of MgO at ab initio level, a hierarchy of model clusters has been devised. The effect of the extended ionic system has been introduced to this localized description by the addition of a point charge (PC) array. Geometry relaxation of the substrate has to some extent been taken into account by optimizing the position of the oxygen ions adjacent to the V-centre. In a preparatory study of the bare (adsorbate free) site the effect of several factors have been compared (quality of basis set, correlation, size and shape of PC-array and of the model clusters). Based on the trends observed the models for the actual study was chosen. Introducing the adsorbate, a purely repulsive interaction was found using the smallest substrate cluster model.

Ab initio investigations of C–H and hydrogen defects in GaAs using a real–space cluster approach

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An understanding of carbon and hydrogen defects within III–V materials is crucial for the fabrication of efficient electronic devices with an adequate operating lifetime using MOCVD grown material. These defects are studied using the highly efficient serial and parallel versions of the local density functional cluster code AIMPRO both on workstations and on the T3D. The use of clusters offers certain advantages over a supercell method. It is found that the energy barrier to the dissociation of the neutral C(As)–H complex is 1.8 eV, but that this is drastically reduced in the presence of minority carriers. The barrier energy for the dissociation of C–H[−] is reduced to less than half of that in the neutral case. This remarkable result explains recent experimental findings on the degradation of GaAs based heterojunction bipolar transistors.

The stability of the possible sites which H occupies in GaAs are investigated. The equilibrium site is found to be on a gallium–arsenic bond axis for H^0 and H^+ but at a Ga anti–bonding site for H^- .

It is also shown that a H_2 molecule is stable and has a lower energy than the two possible H_2^* defects. These molecules could act as a reservoir for H within the material and the presence of interstitial hydrogen in GaAs has recently been experimentally identified as a precursor to the degrading of essential device characteristics. The stability of H_2 over H_2^* is similar to results previously obtained for Si, but contrasts with the situation in diamond.

Proton-ordered ice: periodic models and embedded-cluster study of impurities

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The use of ‘periodic’ models for determining the characteristics and chemical-physical properties of ice is of great interest for two reasons. Firstly, because they allow the taking into account of the cooperative effects of hydrogen bonds and long-range electrostatic interactions in a more complete way than is the case with cluster models. Secondly, they give a crystal solution which can be used for the study of local defects by adopting an embedded-cluster technique.

For this purpose, the adoption of a proton-ordered structure is required, though it is well-known that ice is intrinsically disordered. A proton-ordered structure, which is stable at low pressures and temperatures, has been detected experimentally. It is formed through an order-disorder phase transition of ordinary ice which occurs around $T = 70$ K and is catalyzed by KOH. Nevertheless, this orthorhombic phase of ice, symmetry Cmc21 (C), cannot be used in the study of adsorption phenomena with thin-film models because of the presence of a strong electric dipole moment normal to the surface. We have considered a different ice structure, also orthorhombic but with symmetry Pna21 (P), because it shows only a weak dipole moment parallel to the surface.

In the present work, preliminary results obtained with *ab initio* HF-LCAO methods on the two ice structures C and P are presented. The geometries have been optimized using the CRYSTAL program and a comparison between some bulk and surface properties of the two structures has been carried out. Calculations on the KOH defect in the two phases have been done using the EMBED program. In this way it was intended to verify whether the presence of KOH is fundamental in the formation of a local ordered structure of symmetry C rather than of symmetry P during the phase transition.

Embedded Cluster Modelling of Zeolite Catalysis

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An embedding scheme, designed to accurately model the electrostatic potential within a periodic zeolite is presented. In this model, a hydrogen terminated cluster is embedded within a set of point charges, designed to modify the electrostatic potential of the cluster to accurately represent the electrostatic potential of the periodic system, as derived from a periodic Hartree-Fock wavefunction. The computational implementation of the method is described, with applications to a number of systems of catalytic interest.

Some calculations relevant to Methanol Conversion over Acidic Zeolite Catalysts

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Two reaction pathways for acid catalysed methylation of lattice oxygen centres have been studied using *ab-initio* restricted Hartree-Fock and semi-empirical AM1 methods. Results using a 3-21G basis and a simple H₂O.Al(OH)₃ model for a Brønsted acid site suggest that methylation involving two adsorbed methanol molecules is much more favourable than that involving only one. These results have been explained on the basis of the S_N2 nature and the greater transition state solvation of the route involving two methanols. The semi-empirical AM1 method was found to be unsuitable for study of this methylation reaction.

The effects of periodic boundary conditions on phonon calculations in sodium chloride

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In order to calculate the normal modes of a crystal, the force constants relating ionic displacement and the resulting forces must be found. In the framework of first-principles calculations, this is commonly done by calculating the Hellmann-Feynman forces on all the ions when one ion is displaced, using periodic boundary conditions. The dynamical matrix is then constructed, with the help of the symmetry of the crystal, and diagonalised to give the normal modes.

Two restrictions arise from the use of periodic boundary conditions. Firstly, in finite supercells, the ‘force constants’ found will be linear combinations of the true force constants of a crystal, so in all but very large supercells only phonons with wavevectors equal to the reciprocal lattice vectors of the supercell will be found accurately. Furthermore, periodic boundary conditions also preclude any macroscopic electric field. Since longitudinal optic phonons produce such a field at long wavelengths, splitting between longitudinal and transverse optical phonons near the zone centre will therefore not appear using this method.

We have illustrated these effects by calculating the Γ and X modes of sodium chloride using this simple technique, using density-functional theory in the local density approximation. The lack of LO-TO splitting at Γ is shown, but the displacement of pairs of ions rather than individual ions generates good agreement with experiment at X . The problems involved in calculating the correct longitudinal frequencies and various methods of improving the calculations are discussed, together with steps towards implementing these techniques in existing code.

Modelling of Localised States in Condensed Matter

(Keele, June 14-16, 1995)

Wednesday June 14th

10.00- Registration

13.00-13.45 Coffee/tea

13.45-14.00 Welcome (C.R.A. Catlow and M.J. Gillan)

14.00-15.00 I.V. ABARENKOV*, V.L. Bulatov, R. Godby, V. Heine, M. Payne, A.V. Titov,
I.I. Tupitsyn (* Sankt-Peterburg, Russia)

*Combined density functional and configuration interaction method
for the electronic structure of solids with impurities.*

15.00-16.00 A.H. HARKER (AEA Technology, Harwell, UK)

*A hybrid shell-model/quantum mechanical treatment of defects
in ionic crystals.*

16.00-16.30 Coffee/tea break

16.30-17.30 C. PISANI (University of Torino, Torino, Italy)

The EMBED project: recent results, problems and prospects.

17.30-18.00 U. BIRKENHEUER (University of Torino, Torino, Italy)

*Unrestricted Hartree-Fock method for local defects in crystals
and at their surfaces.*

Thursday June 15th

09.00-10.00 M.J. GILLAN, E. Hernández (University of Keele, Keele, UK)

The relation between embedding and linear scaling.

10.00-11.00 V.A. TELEZHKIN (Donetsk Institute of Physics and Technology of
the Ukrainian Academy of Sciences, Donetsk, Ukraine)

New Tight-Binding Method (Molecule as a Defect of the Hilbert Space).

11.00-11.30 Coffee/tea break

11.30-12.30 D.M. BIRD, S. Crampin, R. James

and J.R. Trail (University of Bath, Bath, UK)

Embedding calculations based on ab initio pseudopotential technique.

12.30-13.00 F. CORÁ*, C.R.A. Catlow, M. Leslie, R. Nada,

R. Orlando, C. Pisani and V.R.Saunders
(* The Royal Institution of Great Britain, London, UK)
*A combination of the Quantum-Mechanical Perturbed-Cluster
and the Semiclassical Mott-Littleton techniques for the study
of charged defects in crystals.*

13.00-14.30 Lunch

14.30-15.30 S. CRAMPIN (University of Bath, Bath, UK)
*Green function methods for surface state scattering
studies and related problems.*

15.30-16.30 P.A. MADDEN (University of Oxford, UK)
Simplified electron energetics in Car-Parrinello MD

16.30-17.00 Coffee/tea break

17.00-18.00 I.H. HILLIER (University of Manchester, Manchester, UK)
Quantum mechanical embedding methods to study solvation.

18.00-18.30 General discussion

18.30-20.00 Wine reception, posters.

20.00 Workshop dinner

Friday June 16th

09.00-10.00 Z. BARANDIARAN (Universidad Autonoma de Madrid, Spain)
*Ab initio model potential (AIMP) embedded-cluster
studies of localised ground and excited states
in ionic crystals.*

10.00-11.00 V. LUAÑA (University of Oviedo, Spain)
Locality in the modelisation and analysis of ionic materials

11.00-11.30 Coffee/tea break

11.30-12.30 L.N. KANTOROVICH (University of Keele, Keele, UK)
*Quantum cluster in polarisable crystal environment.
Consistent microscopical approach.*

12.30-13.00 L. CRUZEIRO-HANSSON (Birkbeck College, London, UK)
*Thermal effects on localised solutions of the
Fröhlich/Holstein/Davydov Hamiltonian.*

13.00-14.00 Lunch

14.00-15.00 B.P. ZAPOL (Latvian University, Riga, Latvia)
*Self-consistent equations and gauge transformations of
electron group functions.*

15.00-15.30 N.M. HARRISON (Daresbury Laboratory, Daresbury, UK)

*Localised states in transition metal insulators; an Hartree Fock
description.*

15.30-16.30 General discussion and closing

Posters should be displayed at the beginning and remain until the end of the workshop.