Theor Chem Acc (2004) 111:246–254
DOI 10.1007/s00214-003-0540-5

Theoretical
Chemistry Accounts

Regular article

Quasi-periodic ab initio models in material science: the case of oxygen-deficient centers in optical fibers

C. Pisani, M. Busso, F. Lopez-Gejo, S. Casassa, L. Maschio

Università INFM di Torino, Sezione F, and Dipartimento di Chimica IFM, Università di Torino, via Giuria 5, 10125 Turin, Italy

Received: 23 January 2003 / Accepted: 30 April 2003 /

Abstract. Ab initio methods for the study of multielectronic systems have become an essential tool also in the field of material science. They can give an invaluable contribution for the analysis and interpretation of experimental results or for the prediction of the properties of new materials. Drastic simplifications must be adopted anyway, owing to the inherent complexity of the systems that are the subjects of these studies. A proper choice of the model (both concerning geometry and level of approximation) is often the most critical step to be taken as concerns the reliability and usefulness of the results, given the variety of techniques available, whose merits and drawbacks are often difficult to assess a priori. The case study of oxygen vacancies in optical fibers serves the purpose of discussing advantages and limitations of one such approaches, based on the perturbed-cluster theory. The perturbed-cluster method consists in first providing a periodic model of the glassy fiber, whose quantum mechanical description can be obtained rather easily, then simulating locally the defective region and studying the processes that occur there through the use of an embedding ab initio technique. The problem is presented, the method adopted and some results obtained are critically analyzed.

Keywords: Silica fiber – Oxygen vacancy – Embedding – Ab initio models

1 Introduction

This paper has been written in honour of Jacopo Tomasi, whose extraordinary activity as a researcher and a teacher has been for many years, and still is, a stimulus and an example to all those operating in the field of theoretical chemistry in Italy and worldwide.

A number of problems in material science concern the dependence of the energetic and electronic properties of the material on the coordinates of the constituent nuclei. The relative stability of different crystalline polymorphs, the catalytic activity of crystalline surfaces, characteristic optical transition energies associated with structural defects or impurities, the magnetic properties of ordered phases, the distribution of vibrational frequencies and the effect of temperature on all these properties are a few examples. Owing to the impressively fast rate at which computational tools are being improved and hardware costs reduced, there is growing interest on the part of material engineers in the computer simulation of these kinds of problems. An appropriate modeling followed by the computational analysis of the model can give an invaluable contribution for the interpretation of experimental results or for the prediction of effects and properties not yet observed or hard to test experimentally. The difficulty here is that the systems to be modeled and the answers to be given are intrinsically complex as a rule, because a large (in the limit, a macroscopically large) number of atoms are involved. We are concerned in the following with a class of problems where a quantum mechanical (QM) description is mandatory; they are at the boundary between the traditional areas of theoretical solid-state physics (they concern condensed phases, often in a quasi-crystalline arrangement) and quantum chemistry (the information to be collected requires detailed knowledge of the electronic structure at a subatomic level).

In order to demonstrate how delicate and controversial the modeling of these problems can be, we shall use as an example a study case in which we have been involved for some years now and which concerns the formation of photorefractive Bragg gratings in germanium-doped silica fibers. The problem is of great technological relevance in the field of optical communication and optical devices, which has been revolutionized since the discovery by Hill et al. [1] that it is possible to inscribe into optical fibers by UV irradiation regular

---

Contribution to the Jacopo Tomasi Honorary

Correspondence to: C. Pisani
e-mail: cesare.pisani@unito.it

patterns (Bragg gratings) where irradiated regions alternate with nonirradiated ones, the two being characterized by a slightly different refractive index. This has permitted the realization of all-optical devices which can act as communication network elements, sensors or lasers (see the recent review article by Othonos and references therein [2]). In spite of intense research, the microscopic mechanisms which are responsible for the change of the refractive index are not yet fully understood, although knowledge of them would be extremely important in order to produce telecommunication devices which are reliable over long periods of time and to optimize their quality [3]. Experimental and theoretical studies generally agree about the hypothesis that at the origin of the fiber transformation is the interaction of the UV radiation with oxygen-deficient centers (ODC) inside the fiber [3, 4, 5]. ODCs are local defects originating from the absence of one [ODC(I)] or two [ODC(II)] of the four oxygen atoms normally coordinated to a "tetrahedral" X atom in silica-like structures (the symbol X or Y are used to indicate either a Si or a Ge atom). Following the absorption of a UV quantum of about 5 eV, an optical transition or ionization takes place at the ODC site, which is believed to trigger a reconstruction process. Since continuous wave laser irradiation is normally used, it has been hypothesized that also two-photon (probably incoherent) absorption processes may occur. The final result is either a decrease of the defectiveness or the accumulation in the irradiated region of a new kind of defect; the associated structural changes can cause a small increase of the refractive index there.

To make this picture more detailed, a number of questions should be answered which can be broadly classified into two main categories and are still a matter of debate. The former concerns the primary process of absorption: the characterization of the initial state and the kind of excitation that occurs there; the latter concerns the process or processes through which the energy accumulated locally is dissipated, leading to the reconstructed structure. Experimental data are abundant but not very informative on a microscopic scale, since they consist principally of absorption–luminescence spectra and in the characteristics of the Bragg grating finally inscribed in the irradiated sample. Furthermore, for technological reasons, a wide variety of silica-based structures have been explored, differing in the mode of production, the type of dopants present (Ge, H, B, etc.) and their concentration; frequency, power, mode of irradiation were also changed in the different studies.

The task of rationalizing this bewildering and sometimes contradictory experimental evidence is far from simple: a large number of microscopic models have been proposed, more often aimed at explaining one or other peculiar aspect than at providing a comprehensive interpretation. Accordingly, QM calculations have been performed based on different approaches and computational tools. In the rest of the paper we shall try to give an idea of these efforts. In particular, the characterization of ODCs and the modeling of the processes which might take place there on irradiation are considered. After providing a broad picture of theoretical work in this area of research (Sect. 2), we go into some details concerning the approach we have been following, based on the so-called perturbed-cluster (PC) theory (Sect. 3). The aim is to illustrate the power and limitations of present-day QM approaches in material science applications, and at the same time to justify the use of a wide spectrum of techniques: exploiting complementary information may be critically important for casting light on "dirty" problems like the one considered here.

2 Problems, models and methods

The material scientist has available from the shelf a variety of powerful tools for the QM simulation of systems and processes of interest; all of them have found application in the study of ODCs. It is outside the scope of this paper to provide a review of such studies; rather, we want to illustrate through recent examples different aspects of the ODC problem and, at the same time, to discuss merits and drawbacks of the various approaches.

The characteristics of the structure that hosts the defect are known to have a relevant role in its photosensitivity properties, but it is not clear why and to what extent. In particular, the question can be asked whether the structural disorder present in glassy fibers is an essential feature for the basic microscopic processes to take place, or if the same kind of behavior can occur in crystalline structures with an adequate concentration of defects. A "statistical" approach to analyzing the role of disorder in the energetics of defects in silica may be found in a recent paper by Szymanski et al. [6], who studied the incorporation of atomic oxygen with the formation of Si–O–O–Si peroxylinkages, using periodic plane-wave density functional theory (PW-DFT) calculations. Their method consists in first generating a periodic model of amorphous silica (a-SiO_2): the unit cell contains 24 formula units, and the position of the atoms inside is obtained by classical molecular dynamics (MD) simulation (more or less rapid quenching from melting), followed by static relaxation using DFT. The cost of incorporating an oxygen atom in the different Si–O–Si bonds was then calculated: a broad range of energies was found, from about 1.1 to 2.7 eV. For comparison, the oxygen incorporation energies in crystalline α-quartz are 2.03 and 2.21 eV. The reason for such a wide spread was searched for by means of a clever analysis of "local" and "long-range" contributions. The two were found to be largely uncorrelated, and the latter to have a dominant role: owing to disorder, the creation of the defect may result with about equal probability in a release or in an increase of the strain in the surrounding structure, even a few bonds apart, in an energy range from about -0.5 to 0.5 eV. Similar results may also be expected as concerns the energy of formation of ODCs in silica and of the related processes. The important message from this study is that neglect of this source of variability may result in the absence of an essential aspect of the defect energetics in disordered structures.

This criticism applies in particular to the cluster model, which is by far the most popular in a variety of applications. In the present context it usually consists in designing a molecule made up of a few XO_2 units saturated at its border with H atoms, and containing at its interior the ODC of interest; it is clear that the effects of structural disorder are concealed by important boundary effects. On the other hand, there are many reasons for the success of this approach: user friendliness, flexibility, computational efficiency, possibility to work at any degree of sophistication of the QM treatment. In particular, the effect of different kinds of dopants on the properties of ODCs may be easily simulated and analyzed; it is well known that photosensitivity is largely due to germanium-related defects [4], and that it can be affected by the presence of boron and sodium impurities [7]. The cluster model has been applied most often to validate hypotheses concerning the generation of ODC-related paramagnetic centers in silica glasses upon UV irradiation, or to propose new ones [8, 9, 10, 11, 12]. The interest in this topic lies in the fact that electron paramagnetic resonance (EPR) experiments on irradiated samples are the only reliable source of microscopic structural information presently available.

As an example, reference can be made to a recent study by Uchino et al. [9] concerning the formation of a neutral paramagnetic center, called Ge E', following UV absorption at a Ge-type ODC(II) in Ge-doped silica glass. This process is experimentally known to occur when the sample is intensely irradiated at 5.16 eV. The model cluster is made of two pieces: the former, $[(OH)_3SiO]_2Ge$, contains the divalent =Ge: ion; the latter, $[(OH)_3Ge]_2O$, is added to consider possible effects of the condensed environment. All the calculations were performed at the Hartree–Fock (HF) level of theory for the ground-state singlet structures, while excitation energies were obtained with time-dependent density-functional response theory (TD DFRT); a 6-311G(d) basis set was used, supplemented with diffuse s and p functions for the TD DFRT calculations; the cluster geometry in the various electronic configurations was fully optimized. After exploring different possibilities, the following sequence of events was hypothesized as the most probable. In the initial configuration, the two moieties are weakly interacting through the respective central Ge and O ions. Laser irradiation excites one of the lone-pair electrons of =Ge: forming a paramagnetic Ge^+ center; the excited electron is trapped by one of the GeO_4 units in the other moiety. Finally, the electron-hole recombination occurs with the formation of two GeO_3 units having an unpaired electron, namely, Ge E' centers, with a modification of the local bonding structure:

$$\begin{aligned}&[(OH)_3SiO]_2Ge^+ + [(OH)_3Ge^-]O[Ge(OH)_3]\\&\longrightarrow [(OH)_3SiO]_2Ge \cdot [OGe(OH)_3] + (OH)_3Ge\ . \qquad (1)\end{aligned}$$

The energetics calculated for this series of processes is compatible with the experiment. According to the authors, this structural conversion mechanism plays a vital role in the refractive index changes of Ge-doped silica glasses induced by high-power UV radiation. However, serious doubts can be cast about this ingenious proposal not only because of the small size of the cluster, but also because there is a lot of arbitrariness in its design, and especially since no constraints are added in the geometrical optimizations as would be imposed by the connection of the boundary atoms to the surroundings. These critical aspects will be reconsidered in the next section.

The cluster model can be improved in many respects in these kinds of applications. On the one hand, the use of very large clusters, as is being made possible by the use of N-scaling techniques [13], can make the boundary effects much less important or even negligible, so permitting the effects of structural disorder to be explored. On the other hand, some form of “embedding” can be adopted to simulate the condensed environment. One such technique, the PC approach, is discussed in detail in the next section. More simply, the constraints imposed by the chemical binding of the cluster to the surroundings can be introduced by keeping the positions of the saturating H atoms fixed while studying local processes [11]. The effects due to polarization of the environment, particularly important when the process investigated involves the creation or removal of charged species, can be taken into account by using the polarizable continuum model proposed and implemented by Tomasi et al. [14]. A different way to embed the QM cluster in a polarizable environment specially suited for the study of defects in highly ionic systems is that adopted by Shluger et al. [15]: the quantum cluster is surrounded by polarizable semiclassical ions; the cations closest to the cluster carry pseudopotentials to prevent spillover of electrons from the quantum zone. Highly promising is the multilevel own N-layered integrated molecular orbital and molecular mechanics technique of Morokuma [16], which permits the use of large clusters while limiting the high-quality QM treatment to the central portion, and is being applied successfully in the study of the chemical properties of silica-based structures [17].

Supercell (SC) simulation techniques, such as adopted in the previously cited study by Szymanski et al. [6], seem to be immune from the problems which affect the cluster model, provided that the SC size is large enough to make interactions between the periodically reproduced defects unimportant. A secondary advantage is that, in a PW-DFT formulation, this technique is ideally suited for combination with Car–Parrinello QM-MD techniques [18], which permit the simulation of temperature effects. The cost to be paid for the use of this powerful approach is that the level of the QM treatment is relatively poor, often limited to a local density approximation. An SC PW-DFT QM-MD approach was used by Donadio et al. [19] to simulate the photo-induced interconversion from ODC(I) to ODC(II) in pure a-SiO_2. The method for generating the glassy host is quite similar to that adopted by Szymanski et al. [6] (see earlier); in the present case, the unit cell contains 32 formula units and an oxygen vacancy is added in the quenching process, resulting in an ODC(I) defect. This defect is then excited from the ground singlet to a triplet state, to simulate the effect of a photon-induced electronic transition. From this configuration, the system can reach with a small activation energy (0.72 eV) a final state where a twofold coordinated Si atom is found instead of two threefold coordinated ones. This part of the process is in a sense the opposite of that described by Eq. (1), except that all species are here neutral. A reactive channel for the ODC(II)$^+$ $\longrightarrow E'$ transformation has also been identified. The authors claim that their simulations provide strong theoretical support for the viability of these interconversions proposed experimentally only on the basis of spectroscopic data [4]. However, it is not clear to what extent their results depend on the specific structure taken as representative of ODC(I) in a-SiO$_2$. The statistical study by Szymanski et al. [6] suggests that a large number of alternative reactive channels could be proposed depending on the short-range and long-range distribution of atoms about the defect.

In summary, a variety of models and techniques have been adopted. The different studies are usually aimed at validating a given hypothesis; owing to the complexity of the system and of the processes involved, the margin of uncertainty that affects these results is still high. More important, it is difficult to assess how many alternative models, perhaps statistically more significant, could be proposed. There is therefore the need for some systematic "basic" information at the cost of oversimplification of the actual situations: in this sense, prototypical studies concerning well-defined defects in well-defined host structures may serve the purpose of assessing the quality of more specific simulations, of discarding certain models, or of suggesting new hypotheses.

3 The PC approach

3.1 Outline of the method

The aim of the PC method is to model isolated defects in crystals while maintaining a full QM (HF or DFT) description of the extended system. This is achieved in two fundamental steps. First, the unperturbed host solid is described using a periodic model, and its wave function is determined by standard techniques. In the second step, a region of the solid is modeled as a cluster, whose microstructure can be modified. The wavefunction inside this region is then recalculated, accounting for the perturbation caused by the presence of the host. The fundamental assumption of the method (which is strictly valid in the limit of small perturbations and/or large clusters) is that the electronic structure outside the defect region, as described by the projected density of states, remains unchanged i.e., the wave function at the boundary of the cluster matches that of the unperturbed host. The formal PC theory is described in Ref. [20] and references therein.

In contrast to molecular cluster models (both isolated and classically embedded), in the PC method electrons are allowed to be transferred between the host and the cluster. Boundary effects that constitute the main limitation of molecular cluster methods in solid-state applications are almost entirely eliminated.

3.2 Periodic models of the fiber

A crucial step for the use of the PC technique is the definition of the host crystal. Sometimes this choice may be obvious, but not in the present case, as was apparent from the discussion in Sect. 2. A disordered host could be simulated by a periodic structure with a large unit cell of the kind used by Szymanski et al. [6]. This choice would be compatible in principle with the PC technique; however, the advantages of that approach are related precisely to the possibility of simulating defects whose range of influence may go far beyond the size of the unit cell of the host crystal. Furthermore, in the spirit of the systematic investigation outlined at the end of Sect. 2, it is better to consider simple, well-characterized crystalline hosts which bear some resemblance with the fiber. In our simulations, two such systems were selected, to be considered as a reference in the rest of this section. The first is all-silica α-quartz, which is the stablest of the silica polymorphs. The second is a mixed Si–Ge hypothetical structure which was characterized in Ref. [23], indicated there as Q$_\alpha$(1/3). This is a fully optimized α-quartz structure where two of the three tetrahedral atoms in the unit cell are Si and one is Ge. This choice is justified by the fact that the 1:3 proportion of Ge dopant is close to that present in the materials used in experiments [7]. The fact must be stressed again that such choices do not allow the influence of medium-range and long-range disorder to be detected. On the other hand, the local bonding structure and the constraints imposed by the connection with the surrounding condensed medium are correctly embodied in the model.

3.3 Selecting the level of the calculation

Once the host system and the defect of interest have been designed, the quality of the PC calculation depends on three computational choices:

1. Type and level of the one-electron ab initio Hamiltonian adopted.
2. Quality of the representative basis set.
3. Cluster size and shape.

In practice, due account must be taken of software limitations and computational costs. Consider first points 1 and 2. It is essential that the host crystal and the defective cluster are treated at the same level of theory, otherwise no proper embedding is possible. However, while the code adopted for solving the host crystal problem, CRYSTAL98 [21], works with any standard kind of one-electron Hamiltonian (HF, or DFT or hybrid schemes of different quality), the EMBED01 code, which implements the PC theory [22], allows for the moment only the use of the HF approximation. Another difference between the two steps of the calculation concerns the possibility to employ high–quality basis sets. It is well known that in condensed system problems the use of diffuse local functions may give rise to instabilities in the self-consistent-field (SCF) procedure. This problem is more annoying in the PC than in the periodic calculations. An essential step of the PC procedure is the correction of the solution for the defective cluster through a coupling term which restores the connection with the surrounding crystalline medium. When rich basis sets are used, this term may extend deeply on both parts of the cluster boundary, and instabilities may set in in the SCF procedure. The use of a more "rigid" set prevents this risk, but the quality of the solution is downgraded. The influence of basis set quality on the description of ODCs was analyzed in Ref. [24] by considering cubic cristobalite as the host system: this was possible owing to the high symmetry of that silica structure. It was found that formation and excitation energies were systematically underestimated (by 1 to 2 eV) when using the STO-3G set, while electronic structure and equilibrium configuration of the defect were satisfactorily described both in the ground singlet and excited triplet state configuration. All examples reported in the following are referred to HF-STO-3G calculations.

As concerns points 3, namely, selecting the appropriate size and shape of the defective cluster, this is a matter of experience and know how. For the study of simple ODCs in silica, all atoms directly perturbed (either substituted, or eliminated, or displaced) should be separated from the boundary by a couple of chemical bonds, at least; it has been found convenient to terminate the cluster with oxygen rather than with *X* atoms. Examples are given in Sect. 5: typical numbers of atoms in the cluster are between 20 and 50.

3.4 PC models of ODCs and related processes

Figure 1 presents schematically a number of local structures inside α-quartz or $Q_\alpha(1/3)$ which can be used to model prototypical types of ODCs and related processes in pure and doped silica. In the following, we comment on them in a sequence.

3.4.1 Central portion of the "defect-free" cluster

This panel shows the reference structure before the defect is created, which must be treated preliminarily to calculate defect formation energies. In $Q_\alpha(1/3)$, *X* may be

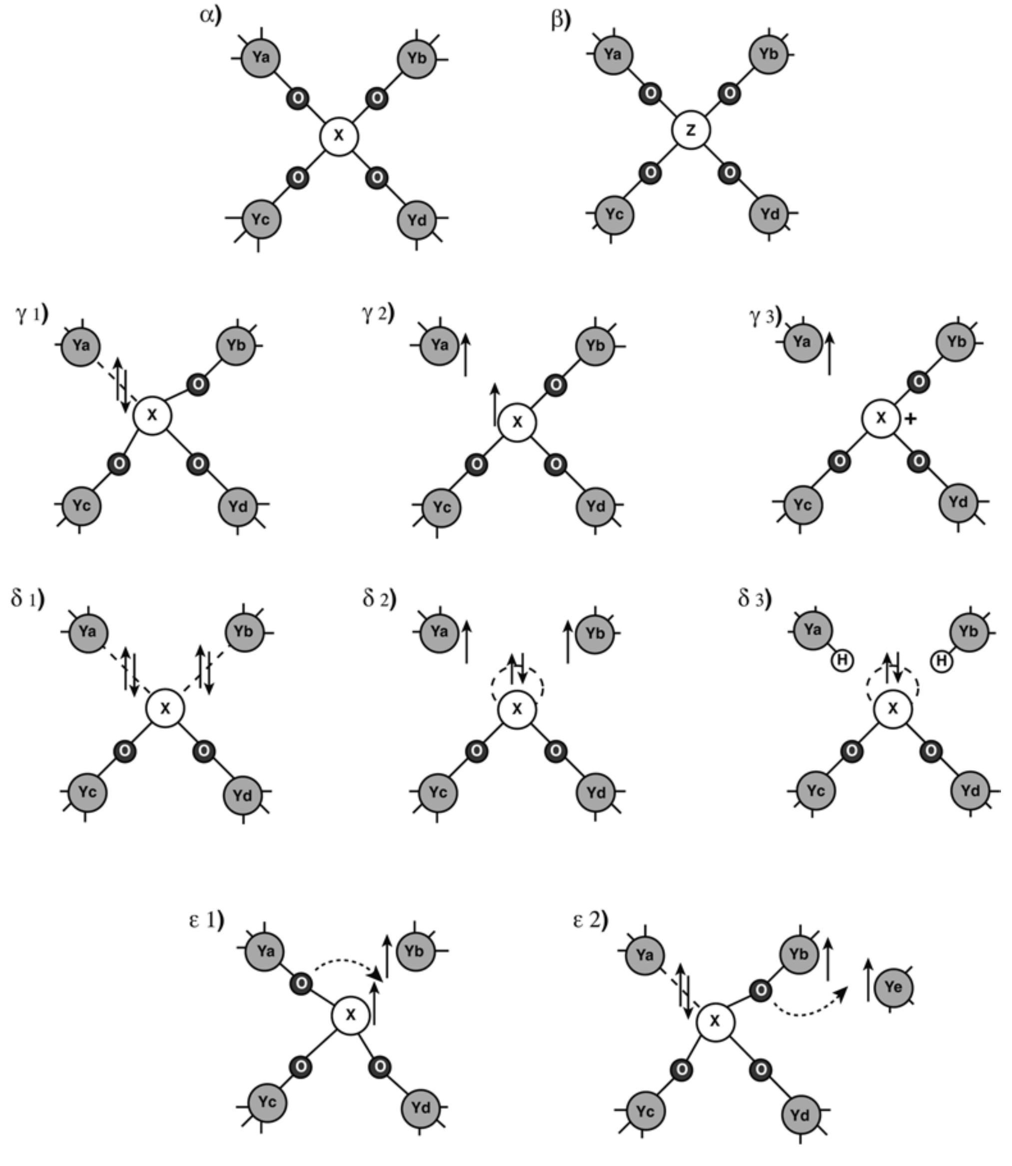

Fig. 1. Schematic representation of local structures in Ge-doped crystalline silica for the modeling of oxygen-deficient centers in optical fibers (see comments in Sect. 3.4). For graphical clarity, the four bonds of the central *X* atom are drawn in a plane

either Si or Ge. In the former case, two of the coordinated tetrahedral Y ions are Si, two are Ge; all bonds are inequivalent. If $X = \mathrm{Ge}$, all Y ions are Si, and the bonds are equivalent in pairs. No Ge–O–Ge bonds may be found in that structure. The actual size of the cluster cut out of the host crystal may be much larger than that here shown, and its shape should be adjusted according to the type of defect or process analyzed (see examples in Sect. 3.5).

3.4.2 Substitutional impurity Z/X

Important primary information can be obtained from this case: energy cost of the substitution, associated geometric and electronic relaxation, etc. Combination with other defect types listed later greatly increases the range of possibilities. In $Q_\alpha(1/3)$, for instance, if $Z/X \equiv \mathrm{Ge/Si}$, the Ge–O–Ge bond can be created and studied. If $Z = \mathrm{B}, \mathrm{P}, \ldots$, the role of hole or electron traps near an ODC can be investigated, etc.

3.4.3 Oxygen vacancy

Eliminating an O atom permits us to model ODC(I), the most frequent type of ODC in optical fibers, and a number of related processes of interest. Some of them have been studied by our group using the PC approach with reference both to pure silica [24, 25] and to Ge-doped silica [26] as the host crystal. The stablest state is a singlet (S), where X and Y^a relax appreciably towards each other to form a weak bond (panel $\gamma 1$). The study of this system permits us to establish both the cost of formation of the vacancy and its preferential location, whether between two Si atoms or near Ge: the latter situation is in fact preferred. Having established the equilibrium configuration of this defect, the adiabatic transition to the first excited singlet (S′) or triplet (T) state can be simulated. The former transition can be related to the experimental observation of a strong absorption peak in the UV spectrum at about 7.6 eV; the latter, to a weak resonance around 4 eV. The T state is particularly interesting (panel $\gamma 2$). Its energy is not very high above the ground state (about 2 eV); since it is relatively long-lived, it may be fairly well populated on irradiation of the sample, and be responsible for some important processes which would be difficult in the singlet ground state. One of them is the so-called puckering transition: one of the two ions near the vacancy (X, say) crosses the plane of the back-bonded oxygens (O^b, O^c, O^d), to reach a metastable “puckered” (P) configuration; the barrier ranges from 1.8 to 2.0 eV, according to the species of the migrating ion [26], and the composition of the host material. P has some notable features: two paramagnetic centers (X and Y^a) are frozen in the system which might be related to the EPR active defects $X\ E'$; furthermore, it has been suggested that the accumulation of P configurations in the irradiated regions could be the main reason for glass densification [27].

The puckering transition could also take place through a two-step process (panel $\gamma 3$), which is presently being characterized in our group. First, on absorption of a light quantum the $X - Y^a$ bond is ionized; the residual electron remains localized on one of the two neighboring species, Y^a, say, while the X charged ion migrates with no appreciable barrier to the plane of its back-bonded oxygens; the resulting defect can be related to the diamagnetic $X(E')^+$ center in optical fibers. When an electron is recaptured, the probabilities of transition to P or to the normal configuration have are comparable.

3.4.4 Twofold coordinated X ion

Creating two oxygen vacancies at the same X ion is the simplest way to model a twofold coordinated ion inside a crystalline silica structure. This can be broadly related to the so-called ODC(II) defect, which is responsible for the strong absorption at about 5.1 eV, and is generally believed to be the site where the densification process is triggered. The ground state is a singlet with two weak X–Y bonds (panel $\delta 1$), but transition to the triplet state (panel $\delta 2$) is much less costly (about 1 eV) than in the ODC(I) case because the Pauli repulsion between the two unpaired electrons on Y^a and Y^b is almost negligible; a lone pair is left on X, which can be then labeled as $=X$:. A number of interesting problems can be studied starting from this basic model. Among them, the following can be mentioned.

The double vacancy site in its triplet configuration might allow the decomposition of the hydrogen molecule (which is often present in silica fibers, and in particular in H-doped ones), with the formation of Y–H bonds which stabilize the $=X$: species (panel $\delta 3$). Preliminary calculations indicate that this process is indeed thermodynamically favored. $=X$: can then rotate to find the equilibrium configuration (see Sect. 3.5); subsequent absorption of a light quantum might lead it to an excited state or to a charged state, with possible transition to new configurations. Note that the initial ODC(II) configuration considered by Uchino et al. [9] (see Sect. 2) would correspond to the case where Y^a and Y^b are both bound to an O atom in front of X. However, the distance between these two atoms in the crystalline lattice (4.8 Å) is far too large to make such chemical bonds possible in the present model.

3.4.5 Oxygen-vacancy migration and clustering

The migration of the vacancy from site to site (for instance, from X–Y^a to X–Y^b: panel $\epsilon 1$) to reach the most favorable configuration may be studied. Preliminary calculations indicate that this is most likely to happen when the system is in a triplet state. The question can also be addressed whether vacancy clustering is likely to occur, i.e., whether a process such as schematically depicted in panel $\epsilon 2$ [starting from two close-by ODC(I) defects, one in a triplet state, and resulting in a $\delta 2$-like defect] is thermodynamically favored or not.

3.5 Discussion of some results

A few processes which might occur at a twofold coordinated X ion in Ge-doped silica $Q_\alpha(1/3)$ are briefly analyzed here to exemplify the kind of PC calculations that can actually be performed and the related

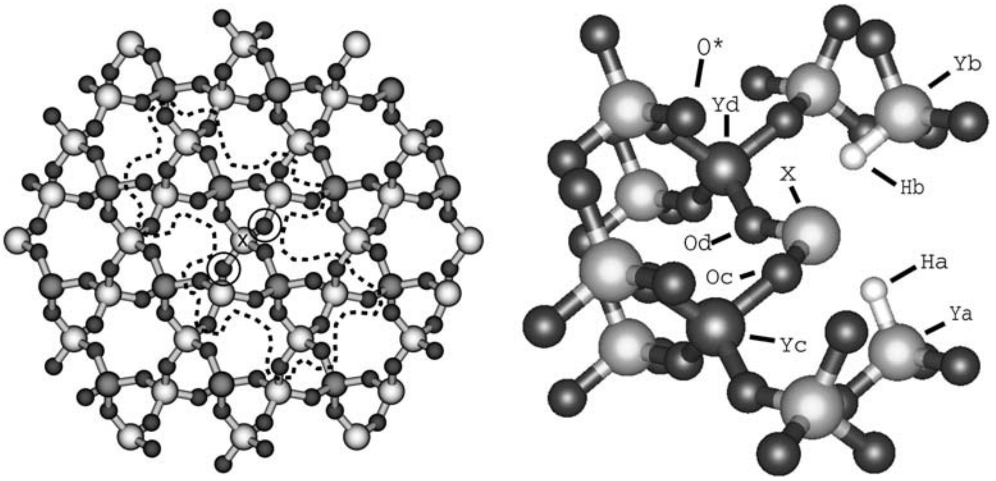

Fig. 2. Embedded clusters adopted in the present perturbed cluster simulations. The *left plot* shows the clusters in the crystalline environment; Si is represented by *light grey*, Ge by *dark grey*, O by *small black spheres*. The small cluster comprises 21 atoms: X, the four-coordinated Y atoms and the oxygens bound to them. The big cluster (enclosed in the *dashed line*) comprises 45 atoms, i.e. in addition to the previous ones, the Si atoms, second neighbors of Y^c and Y^d and the oxygens bound to them. The two removed oxygens are enclosed in a *circle*. The *right plot* shows only the atoms of the big cluster in the case $S^H(0)$, with the labeling of some species of interest

information. They concern the determination of energy, equilibrium geometry and electronic structure of the system for the three situations depicted in Fig. 1, panels $\delta 1$ (ground singlet, S), $\delta 2$ (first excited triplet, T), $\delta 3$ (ground singlet plus saturating hydrogens, S^H). The case will be explicitly treated where X, Y^a and Y^b, are Si ions, while Y^c and Y^d are Ge ions. The two oxygens bound to X, and Y^c, and to X and Y^d, are denoted O^c and O^d, respectively; H^a and H^b are the hydrogen atoms bound to Y^a and Y^b, respectively, in case $\delta 3$.

The two clusters used for the calculations, a "small" (21 atoms) and a "big" one (45 atoms) are shown in Fig. 2: this will help us to illustrate the dependence of the results on cluster size. Both clusters are embedded in the crystalline environment, but electronic structure and nuclear positions are only allowed to relax within the cluster, according to PC theory. In a first step, a constrained geometry optimization is performed, where X can move along the bisector of the O^c–X–O^d angle, while Y^a and Y^b (or H^a and H^b in case $\delta 3$) move along the direction to the missing oxygens. The three resulting configurations of minimum energy are denoted S(0), T(0), $S^H(0)$. In a second step, X is allowed to rotate about the O^c–O^d axis while keeping constant the distance from the two atoms; for any given angle of rotation, θ, the three configurations are $S(\theta)$, $T(\theta)$ and $S^H(\theta)$. Information on the electronic density for some configurations of interest is provided in Figs. 3 and 4; the energy in the three cases as a function of θ is given in Fig. 5. Let us comment briefly on these results.

Consider first the case $\theta = 0$. Figure 3 provides total electron density maps for S(0) and $S^H(0)$. In the scale of the figure, the T(0) map is very similar to the S(0) one. The maps shown were obtained with big-cluster calculations, but on this scale they are not distinguishable from those obtained using the small cluster. More details can be recognized from the difference maps of Fig. 4 (total electron density minus superposition of atomic density). Again, the similarity between the small- and big-cluster results is surprising also in the proximity of the O^* atom, which is included only in the big cluster: this shows both the effectiveness of the embedding procedure adopted and the fact that rearrangement of the electron density takes place essentially in the strict vicinity of X. Two weak X–Y^a and X–Y^b bonds are seen in S(0); correspondingly, the two distances are shorter than in the unrelaxed structure by about 0.3 Å, and the Y^c–X–Y^d angle is reduced from 109 to 99°. In T(0), a lone pair is found on X, and two unpaired electrons on Y^a and Y^b (the Mulliken spin populations on the three atoms are 0.13, 0.59, 0.60 $|e|$, respectively); the distances X–Y^a and X–Y^b become shorter by about 0.15 Å . A similar result is found for $S^H(0)$, except, of course, for the formation of the two Y–H bonds. Incidentally, the calculated energy for the reaction $T(0) + H_2 \longrightarrow S^H(0)$

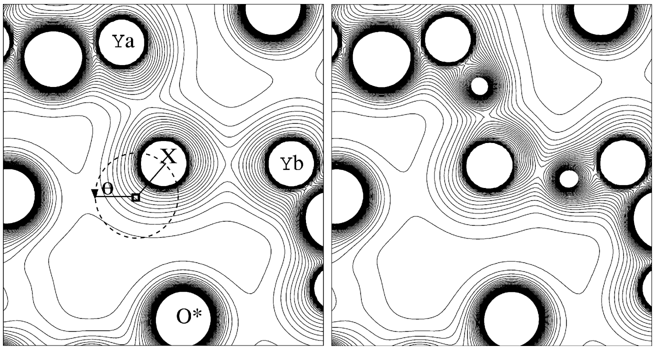

Fig. 3. Total electron density maps for the twofold coordinated silicon for the S(0) (*left*) and $S^H(0)$ (*right*) cases, in the plane defined by the atoms X, Y^a, Y^b. The *small square* identifies the projection on the plane of the figure of the O^c–O^d axis, and the *dashed circle* gives approximately the position of X as a function of θ. Isodensity lines are separated by 0.007 $|e|$ bohr^{-3}; densities larger than 0.2 $|e|$ bohr^{-3} are not represented

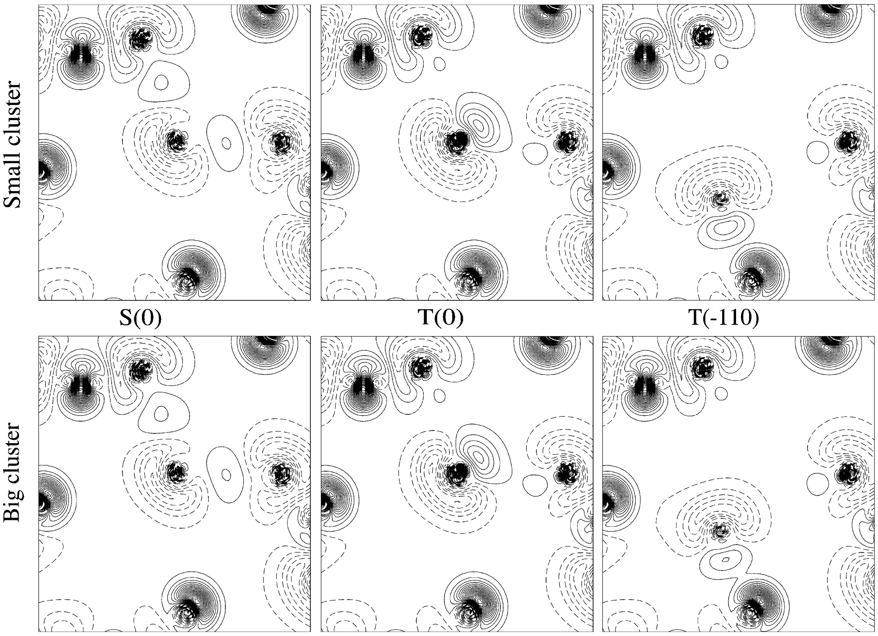

Fig. 4. Difference electron density maps (total minus superposition of atomic densities) for various configurations, as indicated, in the same plane of the Fig. 3. The *top plots* are referred to small-cluster calculations, those *below* to big-cluster calculations. Isodifference lines are separated by 0.007 $|e|$ bohr^{-3}

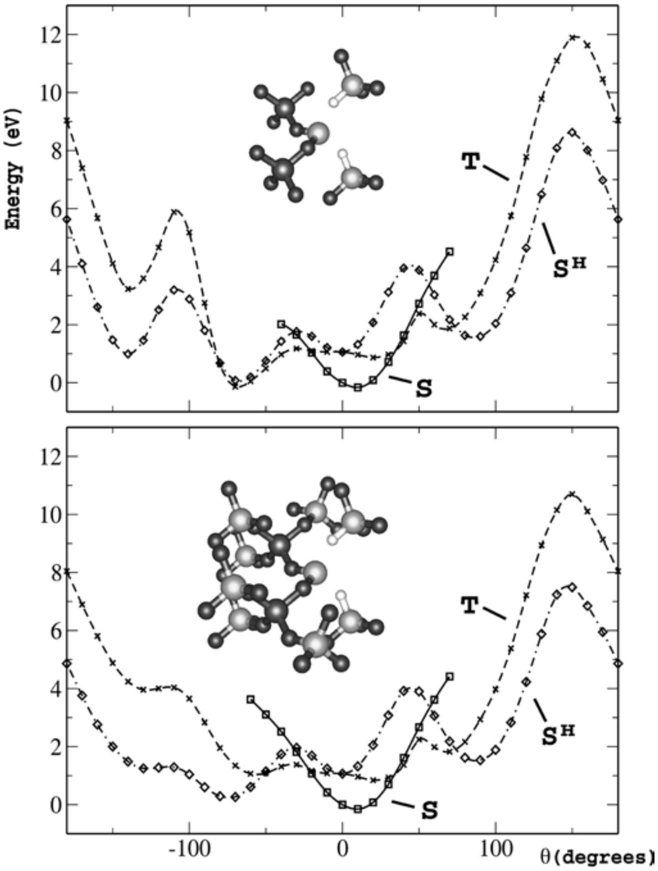

Fig. 5. Energy of the system as a function of the angle, θ, of rotation of the X atom about the O^c–O^d axis for the three configurations: S(θ) (*continuous line*, *squares*), T(θ) (*dashed line*, *crosses*), $S^H(\theta)$ (*dot-dashed line*, *diamonds*), see text for details. The *upper* and *lower panels* correspond to the results obtained with the small and big cluster, respectively. Energies for the S(θ) and T(θ) curves are referred to $E[S(0)] = 0$; the zero of energies for the $S^H(\theta)$ curve is set arbitrarily to make $E[S^H(0)] = E[T(0)]$

is slightly negative; with all the reservations due to the low quality of the basis set, this would imply that a hydrogen molecule can be split when trapped at a defective site like $\delta2$. The energy required for the S(0) $\longrightarrow$ T(0) transition is about 1.5 eV (Fig. 5). This is much lower than that required for a similar transition at an ODC(I) vacancy (3 eV); the reason is that in $\gamma2$ there is an effective Pauli repulsion between the two electrons with parallel spin, which is absent in the $\delta2$ configuration.

The energetics of the constrained rotation of X, represented in Fig. 5 lends itself to some comments. Significant quantitative differences are observed between small- and big-cluster results, in spite of the close similarity of the respective electronic structure. This confirms the finding that the energetics of defects in condensed systems is very sensitive to medium-range and long-range effects. The big cluster employed here is probably still not sufficiently large to warrant that essential convergence has been reached in this respect; this is especially true for the polarization response of the environment, which however, could be estimated semiclassically. On the other hand, serious doubts can be expressed in the light of these results about the energy data from studies using isolated model clusters of moderate size. The $E[S(\theta)]$ curve exhibits simple "parabolic" behavior about $\theta = 10°$; this is due to the progressive distortion (and breaking, eventually) of the weak X–Y^a and X–Y^b bonds. The $E[T(\theta)]$ and $E[S^H(\theta)]$ curves are much more complex and rather similar to each other. Rotation of X implies here no bond-breaking, but rather a different interaction of this ion with respect to the surrounding ones: the corresponding changes of electrostatic and short-range Pauli repulsion forces justify the existence of several maxima and minima. The difference between big- and small-cluster results is specially evident in the region $-150° < \theta < -50°$ where X interacts with a fourth-neighbor oxygen, O*, included in the big, but not in the small, cluster. The polarization response of O*, which is recognizable in the former case in the bottom right plot of Fig. 4, explains the lower energy at the position of closest approach [$\theta = -110°$, $d(X{-}\mathrm{O}^*) = 2.25$ Å] with respect to the small-cluster results.

4 Conclusions and prospects

The QM simulation of complex processes like those occurring at ODCs in glassy materials in the presence of electromagnetic radiation requires taking a number of decisions as concerns the model to be adopted: Is the extended nature of the silica environment incorporated or not? If it is, is its disordered nature, both compositional and structural, taken into account? What level of the QM treatment is chosen? In particular is electron correlation explicitly and accurately estimated? Is the basis set quality adequate?

As we have seen, quite different compromise schemes can be adopted, where the accurate treatment of some aspects requires the use of severe approximations whose influence on the reliability of the results cannot be neglected. The tackling of one specific problem with a variety of approaches can help us to assess the importance of the different effects and to formulate as simple and comprehensive interpretations as possible of the experimental evidence. For example, top-quality simulations with huge clusters (apart from computational costs) would not be very helpful if they cannot allow us to extract the really relevant information.

Embedded-cluster techniques of one kind or another can certainly contribute to this type of analysis; however, in the last decade, comparitively little effort has been devoted to their improvement, both as concerns the level of theory and of computational implementation. The consequence has been that they have become less competitive with respect to other approaches. We feel that this situation may change owing to recent improvements in the computer codes for the treatment of periodic structures [28], which permit the implementation of rigorous and flexible ab initio embedding schemes based on the use of well-localized Wannier functions [29].

Acknowledgements. F. L.-G. is the beneficiary of a two-year post-doctoral bursary in the frame of the Research Training Network "ODUPE" (HPRN-CT-2000-00045). The authors acknowledge the financial contribution of the European Commission through the Human Potential Programme.

References

1. Hill KO, Fujii Y, Johnson, DC, Kawasaki BS (1978) Appl Phys Lett 32: 647
2. Othonos A (1977) Rev Sci Instrum 68: 4309
3. Poumellec B, Kherbouche F (1996) J Phys III 6: 1595
4. Skuja L (1998) J Non-Cryst Solids 239: 16
5. Skuja L (2000) In: Pacchioni G, Skuja L, Griscom DL (eds) Defects in SiO_2 and related dielectrics: Science and Technology. Kluwer, Dordrecht, 73
6. Szymanski MA, Shluger AL, Stoneham AM (2001) Phys Rev B 63: 224207
7. Chiesa M, Ferraris M, Giamello E, Milanese M J Non-Cryst Solids (in press)
8. Uchino T (2001) Curr Opin Solid State Mater Sci 5: 517
9. Uchino T, Takahashi M, Yoko T (2000) Phys Rev Lett 84: 1475
10. Uchino T, Takahashi M, Yoko T (2001) Appl Phys Lett 79: 359
11. Pacchioni G, Ieranò C (1997) J Non-Cryst Solids 216: 1
12. Pacchioni G, Mazzeo C (2000) Phys Rev B 62: 5452
13. (a) Yang W (1991) Phys Rev Lett 66: 438; (b) Yang W, Lee TS (1995) J Chem Phys 103: 5674
14. Tomasi J, Cammi R, Mennucci B (1999) Int J Quantum Chem 75: 783
15. Shluger AL, Sushko PV, Kantorovich LN (1999) Phys Rev B 59: 2417
16. Dapprich S, Komromi I, Byun KS, Morokuma K, Frisch MJ (1999) J Mol Struct (THEOCHEM) 461–462: 1
17. Roggero I, Civalleri B, Ugliengo P (2001) Chem Phys Lett 341: 625
18. Car R, Parrinello M (1985) Phys Rev Lett 55: 2471
19. Donadio D, Bernasconi M, Boero M (2001) Phys Rev Lett 87: 195504
20. Pisani C, Birkenheuer U (1996) Comput Phys Commun 96: 152
21. Dovesi R, Saunders, VR, Roetti C, Causà M, Harrison NM (1999) CRYSTAL98 user's Manual. Technical report. Università di Torino Twin
22. Pisani C, Birkenheuer U, Casassa S, Corà F (2001) EMBED01 user's manual. Technical report. Università di Torino, Twin
23. Lopez-Gejo F, Busso M, Pisani C (2002) J Phys Chem 107. (in press)
24. Sulimov VB, Casassa S, Pisani C, Garapon J, Poumellec B (2000) Modell Simul Mater Sci Eng 8: 763
25. Busso M, Casassa S, Pisani C, Sulimov VB (2002) Modell Simul Mater Sci Eng 10: 21
26. Lopez-Gejo F, Busso M, Maschio L, Pisani C (2003) (submitted)
27. Sulimov VB, Sokolov VO, Dianov EM, Poumellec B (1996) Phys Status Solid (A) 158: 155
28. Zicovich-Wilson CM, Dovesi R, Saunders VR (2001) J Chem Phys 115: 9708
29. Pisani C (2003) J Mol Struct (THEOCHEM) 621: 141