Approximate ab initio simulations of amorphous silicon and glassy chalcogenides

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Abstract

A classic problem of materials theory is to understand the properties of glasses and amorphous materials. Comprehension of disordered systems requires as an initial step atomistic models (coordinates of the atoms) that reproduce the known experimental features of the material. This includes structural (diffraction) information of course, but also higher-order correlations (as from new fluctuation electron microscopy techniques), dynamical information (inelastic neutron scattering, Raman and infrared measurements), electronic and optical information (photoelectron spectroscopy, optical spectra). Models proposed which are jointly in agreement with this array of measurements are likely to enable new insights and we name such models in this paper *realistic*. With such models available, theoretical analysis of properties beside structure becomes appropriate. The electronic and optical properties are commonly of most interest to applications. Such models also enable studies of localization, electron dynamics and other issues of fundamental appeal. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

There has been a great deal of recent activity in the modeling of amorphous and glassy materials. In this paper, we discuss some technical points about obtaining useful models of these important materials and review some important recent developments. This paper focuses on amorphous silicon (a-Si), glassy chalcogenides and some emerging work on the electronic properties of these and other disordered systems.

2. Approaches to modeling amorphous materials

It is a commonly misunderstood point that different methods are needed to secure realistic models of disordered materials depending on the specific chemistry and order of the system. For example, in the case of amorphous Si, there is *no doubt* that the best models are made from a bond switching algorithm, due originally to Wooten, Weaire and Winer [1] (WWW) and extended and modernized by Djordjevic et al. [2]. Models so obtained agree *remarkably well* with structural, vibrational and optical

measurements. Given the apparently ad hoc nature of the WWW procedure, one is led to wonder *why*. Recent work of Barkema and Mousseau [**3] gives a clue to this: the WWW bond switches, appear to *actually happen* frequently in the long time dynamics of a-Si, according to their Activation–Relaxation technique (ART), which is capable of tracking some of these dynamics. Thus it may be that the WWW process is more *physical* than was previously believed. One is tempted to suggest that a scheme like ART plus a reliable potential should be used to *identify* the likely events, then that class of events could be carried out in a generalized WWW-type scheme. Such a procedure might make WWW applicable to binary glasses and other, more complex systems. For disordered systems in general, it is not possible to provide a general failsafe recipe for constructing models of amorphous materials.

In information theory [4], one faces problems of inference commonly of the form: *given incomplete information about a distribution, make an optimal guess for the distribution given the limited information*. When stated this way, it is entirely obvious that one must use all information available to make a 'best guess'. In information theory, there is a variational principle (regularization functional) which picks out a 'best guess' with the variation carried out in a restricted space in which all constraints (e.g. all known information about the distribution) are exactly satisfied. The situation in modeling

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disordered systems is not fundamentally different: *given some (extremely) incomplete experimental information, and energy functional, make a good guess for an atomistic model*. The point here is that one cannot normally use *only* the energy functional and molecular dynamics (MD) to build a useful model—essentially independent information (experimental) exists which is *not directly included* in any attempt to make a model by dynamical simulation.

By the logic of the preceding paragraph, we point out the practical necessity of including a priori information in forming a proper model. The attractive simple idea of 'cook and quench' (e.g., 'melting' then quenching on the computer) to obtain a model without imposing a priori information often *fails* to produce realistic models. The good news is that sometimes very simple and limited application of a priori information is sufficient to make a vast improvement in models. As we discuss below, cook and quench always fails for a-Si, yet a crude method that enforces 4-coordination (WWW method) works brilliantly with a very naïve potential. For systems that compel strong local chemical order and have locally similar topology in the liquid and glass phase (a-SiO$_2$ is the archetype), cook and quench *can* be quite successful. But even here, the simple a priori fact that the anions and cations are homogeneously distributed in space is a necessary assumption. In the same spirit, the successful construction of large realistic models of a-Se appears to require some a priori bias toward a polymeric (chain-like) topology [9]. It *may* be that an impossibly long annealing with a good Hamiltonian would slowly, over time, be able to nucleate the right structures, though the system might in fact crystallize on such long time scales, especially in a small (several hundred atom) super cell model. The system could even conceivably be frustrated in a competition between different amorphous phases (polyamorphism). If a particular amorphous phase is sought, it is both wise and necessary (for millennium MD schemes at least) to build as much a priori information into the initial model as possible. It is well to remember that no method in use simulates the physical process at all realistically, so that *the only meaningful test of a model is its success or failure in reproducing most or all of the experimental information available on the system*.

3. Total energy functionals and forces

Depending on the type of question being asked of a simulation, one can need methods ranging from Keating springs [5] (example: WWW models of a-Si) to Quantum Monte Carlo [6] or Configuration Interaction [7] (example: calculations of defect states which depend sensitively on electron correlation effects). One should select an approach that is sufficiently accurate for the question under consideration and efficient enough to make the calculation possible.

We have found the simplified ab initio local basis

approach of Sankey, 'FIREBALL' [8], to be extremely effective. In fact, we find that in comparison to *experiment*, this Hamiltonian does extremely well, and particularly so for a-Se [9], g-GeSe$_2$ [**10] and g-As$_2$Se$_3$ [11]. This is not a universal guarantee that this scheme will always work (we know for example that it makes significant errors on the energetics of H in c-Si [12] and in some cases in properly representing defect states), but it has proven to be very reliable for the complex amorphous chalcogenide systems mentioned. This is a particular boon since 'full blown' density functional calculations require very expensive approximations, as we discuss below.

When higher accuracy is needed, one can adopt a plane wave code (many are available, including ABINIT [13], as freeware), or a fancier local basis code (SIESTA [14] or FIREBALL2000 [15]). These codes allow for very rich basis sets and gradient corrections to the density functional if needed. One should never lose sight however of the fact that *all* of these codes are *approximate*, and must always be carefully compared to experiment. As a sobering reminder to us all, we recommend the papers of Mitas [16] and coworkers who compared converged density functional, Hartree–Fock and nearly exact quantum Monte Carlo calculations for various carbon clusters and found *important* differences in the energy ordering of structures depending on which (respectable!) method was used.

4. Specific systems

4.1. Amorphous silicon

There is no better cautionary tale for simulators of disordered systems than a-Si [17]. A particularly treacherous feature of the cook and quench approach to modeling a-Si is the ease of obtaining a static structure factor and radial distribution function in good agreement with experiment [18]. The neophyte in this field naturally supposes that such a network is realistic. It turns out however that cook and quench models derived from either classical MD or the very fanciest ab initio MD calculations *fail* to produce networks with reasonable coordination defect densities. Electronic/optical measurements are insistent that the fraction of unpaired spins is tiny—less than 0.1%; typical MD quench schemes obtain between 5 and 20% depending on the potential, simulation parameters, etc., and tend to produce large numbers of five-fold defects, whose very existence is in considerable doubt [19]. Indirect measurements of the electronic density of states yield similar numbers. This range is *totally unacceptable* if one is interested in electronic or optical properties. Yet, the a-Si literature is full of recent papers which have not absorbed the lesson [20]. One can suppose (without proof) that the ultimate root for the failure of MD cook and quench for Si is that a properly equilibrated liquid is a *six-fold* (on average) *metal*, very distinct in all physical

properties from a-Si and on a short time MD time scale impossibly remote from the a-Si topology. Evidently in a topological sense a-Si is much more akin to c-Si in the diamond structure, and it is a wise starting point for WWW to take. The entire spirit of cook and quench is not quite right here in any case, since a-Si is *not* experimentally grown in this way.

As argued above, the WWW scheme is effective for a-Si. The utility of the WWW scheme is not limited to creating homogeneous random network models of a-Si. We [*21,22] have recently made minor modifications to an efficient WWW code of Barkema and Mousseau [23] to model paracrystalline Si (roughly amorphous Si with embedded diamond crystallites), for the first time in agreement with novel fluctuation electron microscopy measurements and electronic/optical measurements (a very small fraction of defects). The nature of the intermediate range order of this material is quite interesting and dependent in controllable ways upon growth condition and thermal treatment. The WWW scheme is also an ideal starting point for forming low defect models of the technologically important a-SiO_2/c-Si interface. Our overall view for Si is then to employ the WWW methods to form a realistic model, then fine tune the structure with a density functional Hamiltonian.

With a realistic model of a-Si courtesy of WWW in hand [2], one can unleash the full power of current electronic structure techniques to much advantage. For example, one can compute the nature of electron states in the gap [19], obtain the nature of the pressure-induced first-order amorphous-to-amorphous transition in a-Si [29], atomistically study doping of the material and begin serious (e.g. based on quantitative computation) study of the Staebler–Wronski effect and the many models which have been proposed to explain light-induced defect creation.

4.2. Chalcogenide glasses

Other systems, such as binary glasses, tend to be more forgiving to brutal cook and quench approaches. These tend to be systems in which the liquid structure and the glass structure are topologically related—composed of similar 'building blocks'—this similarity is connected to the glass forming ability of these materials. Silica and the stoichiometric chalcogenide glasses are examples of this. In these systems, relatively simple potentials have met with considerable success. We suppose that this is because if they are well constructed, they build in this a priori information and get many aspects of the dynamics (and structure) right. For good examples of this, see the paper of P. Vashishta in this volume. In such glasses there are easily identified building blocks (Si–O or Ge–Se tetrahedra in SiO_2 or $GeSe_2$, or $AsSe_3$ pyramids in As_2Se_3), which are highly favored on chemical grounds (a combination of ionicity favoring heteropolar bonding and the 8-N rule).

4.2.1. $GeSe_2$

In 1995 [24] and 1996 [25], we proposed models of g-GeSe2 made with 'FIREBALL [8]'. The resulting models were in uniform agreement with structural, vibrational and electronic measurements on the glasses. We also made models of liquid $GeSe_2$ at this time [26]. The 1996 glass model involved 216 atoms and was subsequently compared to the partial structure factors obtained by Salmon's group using the method of isotopic substitution [**27]. The results are reproduced in Fig. 1 and speak for themselves. A plausible bump appears in the static structure factor near the location of the experimental first sharp diffraction peak (FSDP) and the experimental curves are otherwise very well reproduced. The model is also in pleasing agreement with electronic and optical measurements. Very recently, we performed constant pressure relaxation studies of this model [28] and found that the material had a gradual (not abrupt) pressure-induced insulator-metal transition in stark contrast to a-Si which exhibits a *first-order* transition [29].

This model and a smaller (63 atom) variant [24] was helpful in unraveling the origin of the A_1 and A_{1c} (tetrahedral breathing mode and its 'companion') near the middle of the vibrational spectrum, and essentially confirmed a suggestion [30] that the A_1 mode originated in corner-sharing tetrahedral and the A_{1c} primarily from edge-sharing tetrahedral breathing motions.

4.2.2. Se

Possibly the first amorphous material of interest because of its photo-response was amorphous Se, which was used in early Xerox (photocopy) machines. Because of its classic interest as a light-sensitive material and because of renewed work on a-Se for digital X-ray radiography applications, we made models of a-Se and studied the photo response of the material [9]. To form a satisfactory model of a-Se, we began with a chain-like topology built at random at the proper density of the glass. Fireball was then employed to 'cook and quench' from this starting point which built in the polymeric character of Se bonding in a very crude fashion. The resulting annealed and relaxed network has only one valence alternation pair (3-fold/1-fold) defect in very reasonable agreement with defect concentrations inferred from other measurements. By promoting electrons from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO), one obtains simulated photo-structural rearrangements. It is of interest (with admittedly very limited statistics!) that the most common outcome of the occupation change and subsequent relaxation is 'photo annealing'—an *improved* network as the result of the promotion. This is an interesting contrast to the Staebler–Wronski effect which we approached in a similar way in 1992 [31], and for which new defects tended to result from the promotion rather than an improvement as seen in chalcogenides.
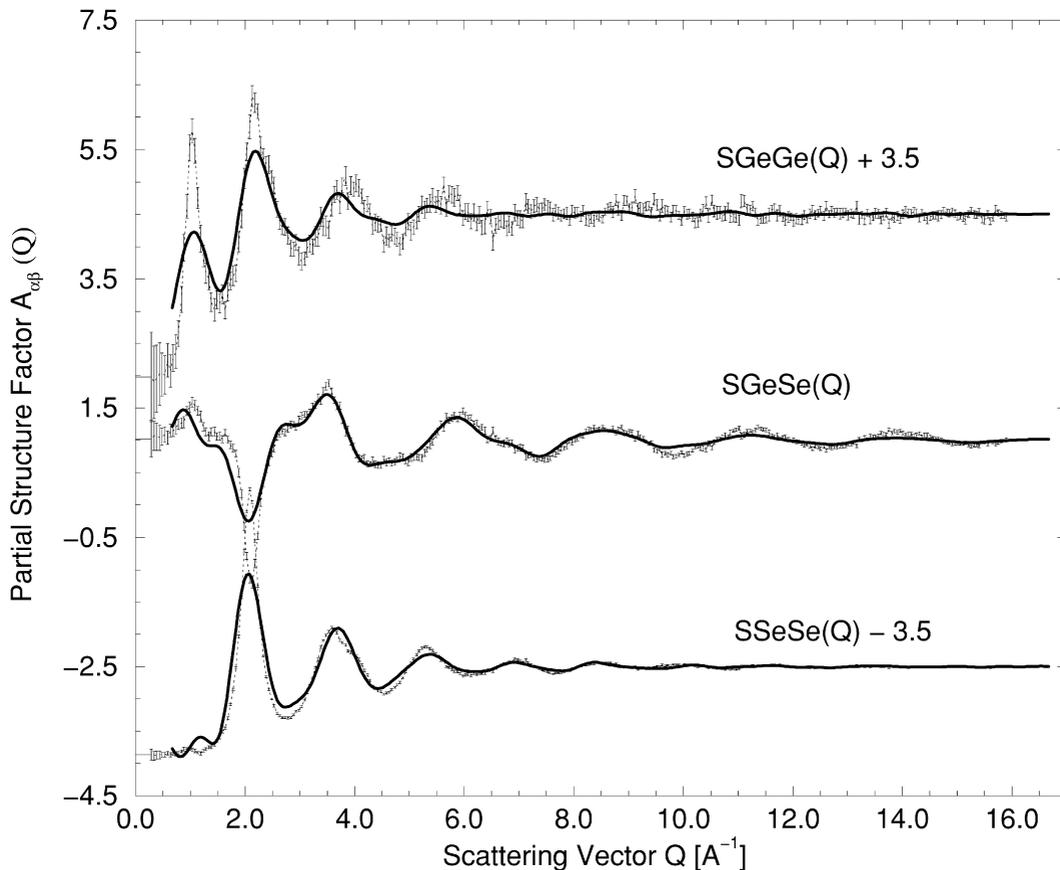
Fig. 1. Partial static structure factors for g-GeSe$_2$: theory and experiment. Experiment [**27] (black curve with error bars) and 216 atom model [25,**10] (solid black curve). The discrepancy between theory and experiment for $Q<2$ Å^{-1} is a finite size artifact.

4.2.3. As$_2$Se$_3$, AsSe

Recently we have also worked on the classic glass former As$_2$Se$_3$ and the closely related technologically interesting material a-AsSe [32]. We have proposed realistic structural models, looked at light-induced structure changes in As$_2$Se$_3$ and compared to careful XPS measurements. In comparing As$_2$Se$_3$ and AsSe, we found it very useful to consider the structural units from which the glasses were composed and compute projected electronic and vibrational state densities onto the constituent units. This provides useful insight into the microstructure of the materials and increases the utility of these experimental spectra as a signature of the different blocks. This utility depends to some extent on how much 'banding' there is between blocks, of course. We refer the reader to the literature for details on these systems.

5. Peculiarities of modeling glasses with Se

Beginning in 1998, Massobrio et al. [33] published an interesting series of papers focusing on the level of approximation needed to model *liquid* GeSe$_2$. They showed that for a plane-wave self-consistent field (SCF) MD simulation, use of the local density approximation (LDA) led to no FSDP as seen in experiment, and an electron density gradient correction (GGA) to the LDA was needed to obtain a network with this feature. The same authors show that the key difference between LDA and GGA is an enhanced ionic character to the bonding for the GGA [34]. It is probable that this effect makes a subtle difference in the local bonding, which affects the intermediate range order, and therefore structure factors for small Q. There is no reason to believe that the GGA *directly* induces network ordering on intermediate length scales. A similar conclusion was drawn by Kirchhoff et al. [35] in careful studies of liquid Se. Thus, it appears that the success of Fireball originates in its use of the Harris functional which yields an enhanced ionicity relative to SCF LDA. Thus, rather unexpectedly, Fireball and expensive rich basis SCF GGA calculations appear to give essentially similar models for disordered GeSe$_2$.

To explore these issues further, we have 'relaxed' a realistic model of elemental a-Se made with FIREBALL with SCF density functional calculations (the excellent local orbital code SIESTA). For each of four increasingly

sophisticated approximations within SIESTA, we performed a conjugate gradient relaxation of the realistic model. A *very* unusual trend was observed: for a minimal basis the local order was ruined, with many one and three-fold atoms, and an unphysically broad first neighbor (FN) peak; at double zeta level, the FN peak split into two distinct peaks, still in poor agreement with experiment. Then, at double zeta with polarization (d) orbitals, the second bump in the FN peak shifted to become a shoulder of the second/third neighbor peak. *Finally, when a GGA was added to this, the original network did not change topology at all and the radial distribution function was in the (original!) excellent agreement with experiment.* It is tempting to suspect that the 'split first neighbor' peak and its dependence upon the approximation used is connected to the FSDP which is at a **Q** value not very different from $2\pi/R$, if R is the distance of the suspect peak.

6. Time dependence and electronic properties [36]

It is of special interest to study the coupling of the lattice and the electron states in disordered materials. We believe that this is a promising emerging frontier in disordered systems since modeling of photo-structural effects and transport depend critically upon the interaction of electrons and phonons. There is always a very large electron-phonon coupling for the localized states in the band tails and in the optical gap. We believe that the work discussed in this section is directly relevant to any system with disorder and therefore (potentially) localized states. This would include glasses, polymers and even transport through molecules. To study these effects on amorphous materials, we have taken three different approaches:

First, we have shown that a reasonable estimate of the electron (n)-phonon (ω) coupling is given by $\Xi_n(\omega) = \Sigma_\alpha \chi_\alpha(\omega)\langle\chi_n|\partial H/\partial R_\alpha|\psi_n\rangle$, where α indexes the 3N vibrational displacements, ω is a classical vibrational normal mode frequency for eigenvector χ, R_α indicates the 3N atomic coordinates, H is the electronic Hamiltonian, and the Hellmann–Feynman matrix element is just $\partial E_n/\partial R_\alpha$ for E_n an electronic energy eigenvalue satisfying $H|\psi_n\rangle = E_n|\psi_n\rangle$. The quantity $\Xi_n(\omega)$ is a trivial byproduct of any calculation of the force constant (Hessian) matrix with finite differences, if one computes $\partial E_n/\partial R_\alpha$ with finite differences at the same time. We find $\Xi_n(\omega)$ to be quite informative, especially in connection with photo structural effects (which require a large electron-phonon coupling). Surface plots of $\Xi_n(\omega)$ for a-Si and a-Se are given elsewhere, and show interesting differences.

Next, we used thermal MD simulation with Born–Oppenheimer dynamics to study electron-lattice effects [*37]. We have shown that there can be dramatic fluctuations in (localized) electron energies and states near the gap. As one would infer from (1), only localized electronic states seem to be strongly modulated by the lattice. This

work is of certain importance to transport. It has the limitation that it keeps an unphysical 'coherence' to the states, since the states are always computed anew at each step and are therefore always 'pure'.

Finally, we have explored direct integration of the time-dependent Schrodinger (Kohn–Sham) equation. As Thomas has suggested [38], an electron starting in some localized state (as for example a donor) will suffer scattering with the phonons and become progressively delocalized with successive scattering events. Thomas has shown with an Anderson model that this 'phonon-induced delocalization' is quite important to understanding transport in amorphous materials. We have shown that his statement is true for models of a-Si and a density functional Hamiltonian. One can understand this as a step toward a 'realistic' solution of the finite-temperature Anderson problem [39].

In a *bit* more detail, we implemented this with a simplified density-functional Hamiltonian (Fireball96) and used a simple direct approach to integrating $i\hbar\partial|\psi_n(t)\rangle/\partial t = H|\psi_n(t)\rangle$ subject to the initial condition $|\psi_n(0)\rangle$ being a suitable starting wave packet, or in practice something like a localized band tail state. As an example, we have computed the time development of the HOMO level in a very small (64 atom) model of a-Si and computed $|\psi_n(t)\rangle$ with Born–Oppenheimer dynamics (at 300 K) for the ions and using the Crank–Nicholson method with the orthogonalization scheme of Tomfohr and Sankey [40]. The diffusion is presented in Fig. 2. It is evident that the thermal disorder is sufficient to cause spatial (and spectral) diffusion of the HOMO state. The result is very different (yielding more extended states) than the results for the 'Born–Oppenheimer HOMO'. Details are given elsewhere [36].

Electronic diffusion is clearly seen, and is easily understood qualitatively as a consequence of quantum mechanical mixing [*41] when another state gets close in energy (and real space) to a reference eigenstate whose evolution we are tracking. The mixing naturally leads to less localized states and this continues in principle until the packet has diffused throughout the simulation cell. Details are given elsewhere [**42].

7. Future prospects

We believe that the future of this area is very promising because: (1) methods of sufficient accuracy and efficiency exist to connect directly to a variety of experiments and even to begin to guide experiment, as the methods (we mean energy functionals *and* simulation regimes collectively) become truly predictive. (2) There are prospects for technological development (examples: fast-ion conductor memory devices, opto-mechanical devices, hosts for rare earth emitters, thin-film devices, photovoltaic applications, etc.). (3) Exciting new physics like the intermediate phase
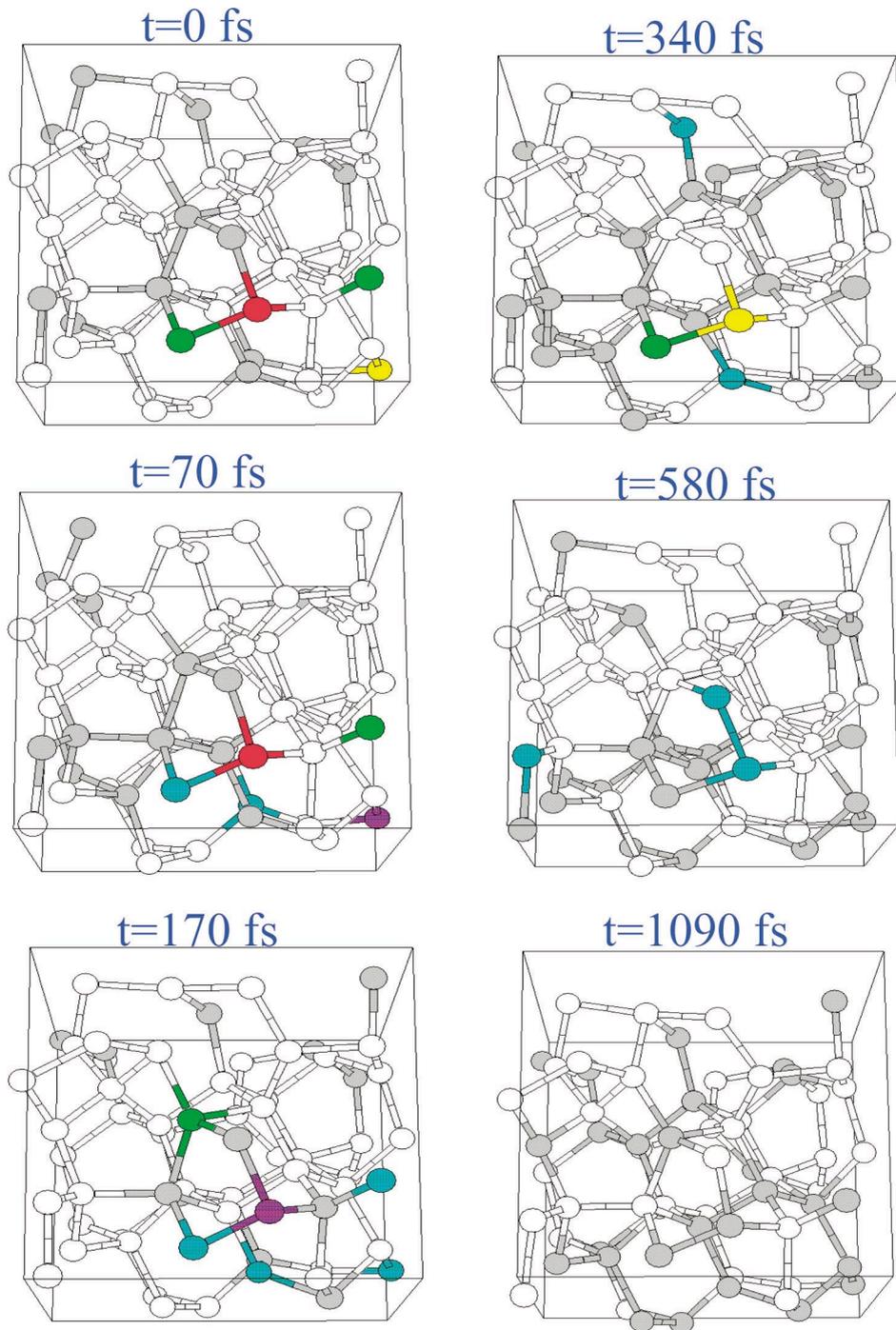
Fig. 2. Time evolution of the HOMO state in a small (64 atom) model of amorphous silicon. The initial condition (upper left corner) is a dangling bond (three-fold atom) with energy near midgap. Ionic temperature is fixed at 300 K. Colors depict varying concentrations of charge with rank red (>0.15 electron), pink, orange, yellow, green blue, grey, white ($<1/64$ electron) in equal increments. Note the nearly uniform dispersion of the state after ca. 500 fs.

[43]. (4) Emerging experimental techniques like fluctuation electron microscopy (FEM), a promising probe of intermediate-range order [44]. We are certain that there are many other promising possibilities.

8. Conclusion

We have discussed several useful models of amorphous materials and approximations which are suited to some of

these. We emphasized the essential role of a priori information in model formation, and the emerging area of electronic properties and associated dependence on temperature.

Acknowledgements

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