ELECTRONIC STRUCTURE METHODS WITH APPLICATIONS TO AMORPHOUS SEMICONDUCTORS

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1. Introduction and Background

The theoretical description of amorphous and glassy materials is a persistent challenge to scientists. The amorphous state possesses many features unknown in other forms of matter. Some unique qualities of glasses include; floppy modes and the associated floppy to rigid transition, other dynamical features such as tunneling modes and two level systems; special electronic character, such as the exponential bandtails (so called Urbach tails in optical measurements), and unusual defect structures and associated electronic signatures associated with the glassy state. A recurring theme of theory work on amorphous systems is the need to handle small energy differences (as between two close but distinct conformations) in an approximate but reliable fashion. This is a challenge even for the most sophisticated methods in current use.

In this paper, I will concentrate on the electronic structure techniques required for modeling amorphous insulators, including electronic structure based molecular dynamics schemes which produce reliable interatomic forces and therefore enable the modeling of glasses with considerable reliability. Naturally electronic structure techniques are required for any study of the electronic states, defect states and optical properties of these materials. The methods which I present in Section 2 range from simple but efficient descriptions of the electronic structure, to state of the art methods which are computationally prohibitive for all but the smallest systems, but are essential for questions involving very high precision or small energy differences.

1.1. THE NEED FOR ELECTRONIC STRUCTURE CALCULATIONS

It is well to observe at this point that the essential complexity of atomistic descriptions of amorphous insulators stems from the complex many-body interactions between the constituent atoms, mediated by the electronic structure of the material. Thus, in amorphous Si, the forces on an atom depend in minute detail upon the local environment (sometimes up to several shells from the reference atom), the location of the Fermi level (a global quantity) and other concepts unique to the electronic structure. Thus, any fundamental approach to evaluating the plausibility of the topology of a network requires an electronic structure calculation, or at least a total energy functional which is known to accurately track the electronic structure. A corollary is that credible first attempts at modeling (for which accurate potentials are not yet available) require the flexibility of an electronic structure approach.

1.2. LINKS TO EXPERIMENT

Some of the most revealing experimental probes of structure, bonding and dynamics (vibrational modes) involve the electronic aspects of the system either directly (as in photoemission measurements, or optical measurements) or indirectly (to the extent that the electronic structure determines the forces, dynamical matrix and therefore vibrations, etc). Thus, a measurement of the density of states by photoemission techniques provides specific spectral information about a state, and in conjunction with electronic structure work on realistic models, may identify the specific structures responsible for the experimental signature, thereby providing microscopic information about the sample.

1.3. A LITTLE HISTORY

Probably the first important electronic structure calculation salient to amorphous insulators was the work of Weaire and Thorpe[1], who explained how an optical gap was possible in the absence of long range order in the quaternary column IV systems a-Si or a-Ge. Using the simplest tight-binding model, it was shown that the local bonding was the key to understanding the basic structure of the electronic density of states. This insight has proven to be robust, and much detailed *local* information has been gleaned from electron sensitive measurements, but little if anything has been learned from this type of study about the longer range properties of the network. Another aspect of the work of Weaire and Thorpe is that one can 'turn the argument around' and to note that the existence of a gap *implies* that electronic effects are spatially local, since the existence of such a gap is precisely the condition needed to justify an exponentially localized generalized Wannier (real-space localized) representation of the electrons[2]. Such Wannier functions can be truncated at the range of several Å in real systems with arbitrarily little loss of accuracy. This turns out to be a key for extending electronic structure methods to very large systems. An explicit recipe for the computation of these functions is given in Section 3.5.

A breakthrough occurred in the middle eighties when Car and Parrinello[3] showed how to combine the accuracy of *ab initio* density functional methods with force calculations and molecular dynamics techniques. This work, and subsequent work by Sankey[4] with a local basis representation for the density functional orbitals, has enabled the theorist to compute credible atomistic models of amorphous solids and make links to forms of experiment previously inaccessible. While this class of methods must not be oversold [there are severe limitations on the size of systems which may be addressed, the length of simulations possible, and the local density approximation (LDA) itself], it is clear that this work is one of the most important achievements for the developing understanding of glassy systems in general. It has also had a dramatic impact on empirical potential calculations[5], and empirical tight-binding calculations, providing microscopic information to produce reasonably dependable functional forms for the total energy and thereby contributing to the impressive empirical force calculations reported here by Vashishta[5] and others.

The rest of this paper will be organized as follows: In Section 2 I describe methods in use on amorphous insulators in increasing level of complexity from electronic structure motivated empirical potentials to the current state of the art. In Section 3 I describe some important developing special topics of particular interest to the amorphous insulator community, the so-called “order N” methods (which enable electronic structure calculations with CPU and memory demand scaling *linearly* with the system size), and therefore allows study of larger models and longer time scales.

2. METHODS

2.1. SEMI-EMPIRICAL POTENTIALS AND ELECTRONIC STRUCTURE

Successful empirical potentials in current use have functional forms which have been tuned to mimic to the maximum possible degree the energies and forces predicted by electronic structure techniques. A typical procedure is to “guess” a functional form with free parameters and to then determine the parameters most consistent with a variety of accurate total energy calculations, and in some cases also by comparing to experiment. If the energy functional was chosen with enough of the “underlying physics”, then the functional can provide a reasonably transferable (translation: correct in a wide variety of local bonding environments) description of the energetics and interatomic forces. The role of the electronic structure calculation here is simply to provide useful information on energetics and forces.

At a practical level, the success of the empirical approaches has been mixed. If such potentials are used carefully, they can answer questions about model systems that are extremely large (an important ingredient of realism not yet directly attainable with *ab initio* techniques). Normally the reliability is connected with limiting the application of the potential to systems which exhibit bonding reasonably close to conformations for which the potential was fit in the first place. In an extremely disordered environment (such as liquid Si or C), it seems unlikely that an empirical potential will offer a very satisfactory treatment of structure and particularly of *dynamics* in the near future. An excellent review of work in this area has been provided by Carlsson[6].

A recent development of interest is work of Ercolessi[7] who has developed an efficient scheme for computing empirical potentials based upon a "force matching" method. The idea is to take an enormous number of configurations for which the forces are accurately known (from an *ab initio* calculation), (as for example from a thermal simulation representative of the type of study planned for the desired potential), and then minimize the error in the forces predicted potential relative to the forces from the *ab initio* database. If a suitable functional form is selected in the first place, it has been found possible to reduce the error in the potential to acceptable levels. Such an approach has the appealing property that one can partly gauge its accuracy by considering the deviation of the potential from the *ab initio* results. Also there is likely to be "importance sampling" if a thermal simulation is used to form the database. So far, this procedure has been applied to Al[7]; work is in progress for a C potential; a much more challenging area , since the C-C interaction involves both sp^2 and sp^3 bonding, and these states are nearly degenerate.

2.2. EMPIRICAL TIGHT BINDING

The simplest explicit electronic structure calculation is the "empirical tight-binding (ETB) approximation", in which we imagine that the electronic eigenstates can be represented by a linear combination of atomic orbitals: $|\psi_i\rangle = \sum_\mu a^i_\mu |\mu\rangle$ where μ is a site-orbital index and i indexes the state (eigenvector). This method enables the calculation of an approximate one-body Hamiltonian matrix, whose eigenvalues are taken to approximate the allowed electronic energies and the eigenvectors are the states. In the usual implementation of ETB calculations, the basis is taken to be orthonormal: $\langle\mu|\nu\rangle = \delta_{\mu\nu}$. Also, most ETB Hamiltonians include interactions only with nearest neighbors and include only two-center contributions. The sum of the occupied eigenvalues is the (attractive) electronic contribution to the total energy. To compute the system (ions + electrons) energy a repulsive interaction must be added to the electronic part. This is obtained from some fitting procedure. ETB is the simplest approach enabling an estimate of the many-body forces characteristic of covalently bonded materials.

I outline here how an ETB calculation is implemented, since it is simple and is illustrative of many of the concepts of electronic structure calculations in amorphous solids.

(1) We begin by considering a supercell model (large unit cell with periodic boundary conditions) of an amorphous solid with N atoms and atomic coordinates $\{\mathbf{R}_i\}_{i=1}^N$ and three lattice vectors specifying the periodic boundary conditions. We can view the $\{\mathbf{R}_i\}_{i=1}^N$ as specifying a set of "basis vectors" for a crystal with a very large and topologically complex unit cell. Such a large unit cell possesses a band structure, as does any periodic system, but since the cell is supposed to represent an *amorphous* system, it must be large to have credibility. We will suppose that the $\mathbf{k}$ dispersion is negligible because of the large cell size. In calculations *this point must be checked*. The significance of this is discussed further in Section 3.1. We limit our discussion here to the $\mathbf{k} = \mathbf{0}$ point of the Brillouin zone, valid for a large enough model.

(2) Next, we set up the Hamiltonian matrix $H_{\mu\nu} = \langle\mu|\hat{H}|\nu\rangle$ where $\hat{H}$ is the Hamiltonian operator and $|\mu\rangle$ are a set of orbitals (typically s,p_x,p_y, and p_z for a column IV material) centered on each atom. As the matrix elements in this representation depend in detail on the network topology, it is convenient to work with "molecular coordinates" specifying the interatomic hopping. These are V_{ss}, $\mathrm{V}_{sp-\sigma}$, $\mathrm{V}_{pp-\sigma}$, $\mathrm{V}_{pp-\pi}$, in the usual chemistry nomenclature for an sp^3 model. Explicit forms for the distance dependence of these interactions (see for example Harrison[8]) plus simple rules[9] connecting the molecular and $|\mu\rangle$ representation enables the calculation of $\hat{H}$ in the $|\mu\rangle$ representation. The H matrix eigenvalue problem then reads $H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$, the usual orthogonal eigenvalue problem, where the electronic eigenvalues are supposed to be approximated by ϵ_i. For electronic state density calculations or questions of the spectral signature of a defect, an exact diagonalization of H is sufficient.

(3) The calculation of forces is easy when we possess the exact eigenvalues and eigenvectors; then the Hellman-Feynman theorem can be employed in the form:

$$\mathbf{F}_\alpha \;=\; -2\,\partial \sum_{i\ occ} \langle\psi_i|H|\psi_i\rangle/\partial\mathbf{R}_\alpha = 2\sum_{i\ occ}\langle\psi_i| - \partial H/\partial\mathbf{R}_\alpha|\psi_i\rangle \qquad (1)$$

Here, the sum on i is restricted to occupied states. Since total energies, forces, charge densities and other ground state properties depend upon the *occupied* eigenfunctions and eigenvalues, it is natural at this point to introduce the single-particle density operator $\hat{\rho} = \sum_{i\ occ} |\psi_i\rangle\langle\psi_i|$, which in this context is just the projector onto the occupied subspace. In a particular representation $|\mu\rangle$, this is just the usual density matrix:

$$\rho_{\mu\nu} = 2 \sum_{i\ occ} \langle\mu|\psi_i\rangle\langle\psi_i|\nu\rangle \tag{2}$$

giving the usual expression for the electronic energy, $E = \mathrm{Tr}(\rho H)$, and the forces are:

$$\mathbf{F}_\alpha \;=\; -\sum_{\mu\nu} \rho_{\mu\nu}\ \partial H_{\nu\mu}/\partial \mathbf{R}_\alpha \tag{3}$$

We will have more to say about density matrix methods in Section 3.5. Note that this form assumes that the overlap matrix remains exactly the unit matrix through any atomic motions, which is suggestive of why forces in particular are sensitive to the assumption of orthogonality. It is also important to remind the reader that Eq. (3) prescribes only the (purely attractive) electronic part of the force; an additional empirical repulsive pair potential must be added to the electronic energy to specify a system energy; the derivative of this term contributes likewise to the forces, and a dynamical simulation is a complicated balancing act between the electronic and repulsive terms. Atomic trajectories are obtained by integrating the (classical) equations of motion for the atoms using one of many schemes for performing numerical integrations.

For the study of bandtails in amorphous Si the tight-binding model is sometimes used in conjunction with Bethe lattice[10] methods. In this approach, a small cluster (involving typically from several to $\approx$ 20 atoms) is studied, and the cluster is terminated artificially by an infinite network saturating each surface bond in a tight- binding sense, and with each saturating bond being connected to an infinite non-interacting "lattice" of "atoms". Because of its peculiar non-crossing topology, each Bethe tree is isomorphic to a one dimensional problem, so that with Green's function and transfer matrix techniques, this problem can be solved exactly. Such calculations provide useful insight into the formation of defect/bandtail states as a function of bond angle distortion[10, 11], and also to indicate the spectral signature of specific defects (like dangling vs floating (five-fold) bonds).

As to the question of specific ETB Hamiltonians "on the market", there are several, and their transferability is variable. In particular, some are designed for producing good band structures[12], but are at the same time quite inappropriate for total energies and forces. As with the empirical potential methods, these Hamiltonians are most reliable for conformations "near" what the Hamiltonian was fit to in the first place. The entire underlying idea of an orthogonal TB model is the notion that there exist some underlying set of generalized Wannier functions with the property that these are mutually orthonormal in real-space. This is a justified point of view, which, however is valid only for a particular topology – if a different structure is considered, another set of Wannier functions emerge, and the justification for an orthogonal basis fails (unless the Hamiltonian is refit to the new structure). To be fair, it is probable that the failure is not serious until significant distortions are introduced; such is often the case in amorphous insulators. The most widely used ETB Hamiltonians for force calculations are those of Goodwin-Skinner-Pettifor[13] type. The original [13] was for Si; this was adapted by Xu *et al.*[14] to carbon systems. The difficulties with the orthogonal Hamiltonians seem to emerge most dramatically in *force* calculations [a universal feature of simulations is that the forces are more sensitive to approximations than quantities like the energy]. A specific discussion of this point is given in Ref. [15, 16].

More consistently reliable results can be obtained from a variety of nonorthogonal Hamiltonians. Menon[17] has proposed an empirical, nonorthogonal TB Hamiltonian which has been applied widely to clusters and recently has been generalized to bulk systems. Also in this category is a Hamiltonian whose form is motivated by density functional theory, explicitly using squeezed atomic orbitals as basis functions[18]. This Hamiltonian has been tested extensively on total energies and equilibrium structures of simple structures[19], and neglects three-center integrals. Both of these methods seem to provide reasonably faithful descriptions of the chemistry while paying only a slightly higher price than the orthogonal Hamiltonian (the only computational difference is that the "generalized eigenvalue problem": $H|\psi\rangle = \epsilon S|\psi\rangle$, where H, S are the Hamiltonian and basis positive-definite overlap matrix, respectively, and ϵ is the energy eigenvalue).

2.3. GENERAL COMMENTS ON EMPIRICAL METHODS

As a closing note on the semiempirical methods discussed in this paper, we remind the reader *not* to be impressed by large numbers of fitting parameters for either empirical potentials or tight-binding models. Too often, functional forms without much physical basis are "forced" upon the existing information about a material. Then, by construction, the function reproduces *what it was fit to* very well, but sometimes fails spectacularly for questions that don't seem so different from the fitted database. This is the famous "Ockham's razor" principle, telling us roughly that we should use the simplest representation while accounting for as many facts as reproducibly as possible. Thus, some comparatively simple potentials have been quite successful (for example Vashishta's SiO_2 model potential), while I know of at least one empirical potential for elemental Si which has 36 free parameters, which has difficulty with some of the smallest Si clusters, though this is where much of the fitting data came from. Exactly the same case arises for ETB models which, at the initial step, have much of the underlying physics removed (for example by the assumption of perfect orthogonality). Then an attempt is made to patch this assumption up, which can be difficult. Note that these comments are *not* a general indictment of empirical methods; only a cautionary note that the empirical potentials and Hamiltonians must be carefully and sensibly constructed and applied, and attention must be paid to verifying that the method is not being applied to a system more complex than it can handle. For an interesting *quantitative* measure of Ockham's principle, I refer the reader to the Bayesian probability theory literature[20].

2.4. DENSITY FUNCTIONAL THEORY

As we discussed above, the complexity of electronic structure and force calculations arises from the many-body nature of the interactions between the electrons. Currently, it would seem that direct attacks on the many-electron problem is too difficult to have direct impact on amorphous systems, requiring as they do a large number of atoms to provide a model worth investigating. Thus, all the successful electronic structure calculations salient to amorphous insulators have involved some kind of mapping of the many-body problem into an effective one-electron problem. Historically, the Hartree and Hartree-Fock approaches were the first success in this direction; descendants of these methods are widely used today, particularly in quantum chemistry. The ETB work captures some of the many-body effects, albeit in an approximate fashion, and the exact connection between the ETB model and the real many-body problem is obscure.

Of course, the true many-body Hamiltonian treats both the ions and electrons on a quantum mechanical basis. Because of the large mass difference between the electrons and nuclei, it is standard to decouple the nuclear and electronic degrees of freedom with the adiabatic or Born-Oppenheimer approximation[21], in which the electrons are assumed to respond instantly to motions of the ions (the electrons are taken to be in their ground state for all instantaneous ionic conformations). Moreover, the nuclei are treated as classical particles which move in a potential determined by the electrons in their ground state (computed for the given ionic coordinates). For most studies of amorphous solids, this is a reliable approximation, and I am unaware of any such calculation which has not started with the Born-Oppenheimer approximation.

For atomistic force calculations on solids, the current method of choice is density functional theory, due to Kohn, Hohenberg and Sham[22]. Its name comes from its predicted connection between the total ground state electronic energy of a system and the electronic charge density. The following rigorous statements embody the foundation of zero-temperature DFT:

(1) The ground state energy of a many electron system is a functional of the electron density $\rho(\mathbf{x})$:

$$E[\rho] \;=\; \int d^3x V(\mathbf{x})\rho(\mathbf{x}) \;+\; F[\rho], \tag{4}$$

where V is an external potential (due for example to interaction with ions, external fields, e.g., *not* with electrons), and $F[\rho]$ is a *universal* functional of the density. The trouble is that $F[\rho]$ is not exactly known, though there is continuing work to determine it[23]. The practical utility of this result stems from:

(2) The functional $E[\rho]$ is minimized by the true ground state density.

It remains to estimate the functional $F[\rho]$, which in conjunction with the variational principle (2), enables real calculations. To estimate $F[\rho]$, the usual procedure is to note that we already know some of the major contributions to $F[\rho]$, and decompose the functional in the form:

$$F[\rho] = e^2/2 \int d^3x d^3x' \rho(\mathbf{x})\rho(\mathbf{x}')/|\mathbf{x}-\mathbf{x}'| + T_{ni}(\rho) + E_{xc}(\rho) \tag{5}$$

Here, the integral is just the electrostatic (Hartree) interaction of the electrons, T_{ni} is the kinetic energy of a *noninteracting* electron gas of density ρ, and $E_{xc}(\rho)$ is yet another unknown functional, called the "exchange-correlation" functional, which includes nonclassical effects of the interacting electrons. Eq. 5 is difficult to evaluate directly in terms of ρ (because of the term T_{ni}). Thus, one introduces single electron orbitals $|\chi_i\rangle$, for which $T_{ni} = \sum_{i\ occ} \langle\chi_i| - \hbar^2/2m\nabla^2|\chi_i\rangle$, and $\rho = \sum_{i\ occ} |\chi_i(\mathbf{x})|^2$ is the charge density of the physically relevant *interacting* system. The value of this decomposition is that $E_{xc}(\rho)$ is a smoothly and reasonably slowly varying functional of the density: we have included the most difficult and rapidly varying parts of F in T_{ni} and the Hartree integral, as can be seen from essentially exact many-body calculations on the homogeneous electron gas[24]. The Hartree and non-interacting kinetic energy terms are easy to compute and if one makes the "local density approximation" (taking the electron density to be *locally* uniform), and using the results for the homogeneous electron gas, functional (Eq. 5) is fully specified.

With noninteracting orbitals $|\chi_i\rangle$, (with $\rho(\mathbf{x}) = 2\sum_{i\ occ} |\langle\mathbf{x}|\chi_i\rangle|^2$), then the minimum principle plus the constraint that $\langle\chi_i|\chi_j\rangle = \delta_{ij}$ can be translated into an eigenvalue problem for the $|\chi_i\rangle$:

$$\{-\hbar^2\nabla^2/2m + V_{\text{eff}}[\rho(\mathbf{x})]\}|\chi_i\rangle = \epsilon_i|\chi_i\rangle, \tag{6}$$

where the effective (density) dependent potential V_{eff} (in practical calculations orbital dependent) is:

$$V_{\text{eff}}[\rho(\mathbf{x})] = V(\mathbf{x}) + e^2 \int d^3x' \rho(\mathbf{x}')/|\mathbf{x} - \mathbf{x}'| + \delta\epsilon_{xc}/\delta\rho \tag{7}$$

In this equation ϵ_{xc} is the parameterized exchange-correlation energy density from the homogeneous electron gas. The quantities to be considered as physical in local density functional calculations are: the total energy (electronic or system), the ground state electronic charge density $\rho(\mathbf{x})$, and related ground state properties like the forces. In particular, it is tempting to interpret the $|\chi_i\rangle$ and ϵ_i as genuine electronic eigenstates and energies (and indeed this can often be useful); such identifications are not rigorous. It is instructive to note that the starting point of density functional theory was to depart from the use of orbitals and formulate the electronic structure problem rigorously in terms of the electron density ρ; yet a practical implementation (which enables an accurate estimate of the electronic kinetic energy) led us immediately back to orbitals! This illustrates why it would be very worthwhile to know $F(\rho)$, or at least the kinetic energy functional since we would then have a theory with a structure close to Thomas-Fermi form and would therefore be able to seek *one* function ρ rather than the cumbersome collection of orthonormal $|\chi_i\rangle$.

According to the usual application of the variational principle, we err as minimally as possible because of incompleteness in the basis, but of course the representation selected to represent the $|\chi_i\rangle$ must be able to reasonably approximate ρ for reliable results. Of course, the more fundamental assumption of the LDA can itself cause trouble (this is discussed further at the beginning of Section 2.5).

The usual implementation of LDA leads to a nonlinear set of coupled integrodifferential equations. The origin of this nonlinearity is that V_{eff} in the Schrödinger-like (Eq. 6) is ρ-dependent, which in turn depends on the eigenvectors $|\chi_i\rangle$, which in turn depend on V_{eff} and so on. This nonlinearity is dealt with in the usual way "iterating to self consistency", an expensive inner loop on an already challenging computational task.

Consistent with chemical intuition, a minimal basis set of s and p functions is primarily responsible for the bonding and ground state electronic properties. The pseudopotentials are introduced so that only the really relevant electrons, namely the valence orbitals are *explicitly* treated in the calculation. Thus the valence electrons in the LDA solid are interacting with each other and with the ions via exotic potentials mimicking the nucleus dressed with the core electrons. This is an excellent approximation for most applications in the area of amorphous insulators. Pseudopotentials themselves have developed a considerable lore, and the classic modern work in the area is the paper of Bachelet, Hamann and Schlüter[25]. The choice of pseudopotential is governed partly by the basis used: for plane-waves special "soft" pseudopotentials are needed[26, 27]; plane-wave calculations also require a special "separable" form, enabling a factorization that saves considerable computational effort[28] to reduce the number of plane-waves needed; real-space basis functions are immune to this problem.

The next two subsections focus on two heavily used practical implementations of LDA; the first with a basis local in real-space, the second local in momentum space.

2.4.1. *Local basis: "Ab initio Tight Binding"*

Because of formal similarity to the ETB method of Section 2.2, I begin by describing a spatially local basis approach to construct the density functional orbitals $|\chi_i\rangle$. This is a program that was developed by Sankey[4], and his coworkers, and has been extensively applied to studies of amorphous materials.

The essential approximations are: (1) the LDA; (2) nonlocal (angular momentum dependent), norm-conserving pseudopotentials; (3) a minimal basis set of valence orbitals per site (this has recently been extended by Yang[29] to include d states in the basis). These basis functions are slightly excited (confined) pseudoatomic orbitals (PAO) (a PAO is a valence eigenfunction for a given atom type in free space, calculated self consistently within the LDA using pseudopotentials to eliminate the core: in the case of Si, the PAO's can be thought of as approximate atomic 3s and 3p levels); (4) A linearized (non self consistent) version of density functional theory, the "Harris functional"[30] is used which enables calculations without self consistent iterations. This approximation is best discussed by Foulkes and Haydock[31] and is quite remarkably good except in the most ionic systems like SiO_2. For additional discussion see the work of Smith[32].

The use of PAO's is appealing, because the chemistry is naturally built into the basis functions. The payoff is that for materials like Si and C, a minimal basis of four orbitals per site can be used, so that in a model with N atoms, the overlap and Hamiltonian matrix has dimension $n_b N$, for $n_b = 4$ or 9, the number of basis functions per atom (sp or spd) whereas $n_b \approx 100 - 1000$ for many plane-wave calculations (depending in detail on how carefully such a plane-wave calculation is implemented, and how 'hard' the pseudopotential is, which determines the number of plane-waves needed). Also the eigenvectors are expressed naturally in terms of the local PAO's, which is helpful in interpreting the physical meaning of the results. Finally, since the method is implemented entirely in *real-space*, no artificial periodicity is ever imposed, making the approach much more amenable to surface and cluster calculations, where desired.

Sankey and coworkers constructed this method to optimize performance for *ab initio* molecular dynamics simulations; the details are well beyond the scope of this paper. The method is able to handle systems with up to ≈ 500 atoms with exact diagonalization on a workstation, and has been extended recently to include quantum order N methods (see Section 3 below). The ability to perform exact diagonalizations (as opposed to "iterative minimization" schemes) is valuable for systems with states in the gap and particularly metallic systems. The limitation of non self consistency has been lifted recently by Demkov *et al*[33] and Ordejón *et al.*[34]

While this approach is relatively easy to understand, it is vastly more complex than the ETB method above. In particular, to make the scheme efficient, all the two and three-center matrix elements have to be tabled, so no integrals have to be computed during an electronic structure calculation or MD simulation; rather many calls are made to one and two dimensional interpolators. The calculations of forces, particularly with respect to the exchange correlation interaction, is tedious, and "Pulay corrections" must obviously be included, since the basis functions move with the atoms. The formal expressions for matrix elements, forces etc. are substantially more complex than for plane-wave pseudopotential methods of the next Section. I refer the reader particularly to References [4, 33, 34] for the details of the theory. This scheme has found considerable use in amorphous insulators.

2.4.2. *Plane-waves: Car-Parrinello methods*

The first *ab initio* molecular dynamics simulation was performed in 1985 by Car and Parrinello (CP). I begin with a comment on what "CP" means. Often a "CP simulation" refers to a molecular dynamics calculation using a plane wave basis and an iterative minimization scheme to solve the electronic structure problem (the self consistent LDA equations). More properly, "CP" refers only to a method for coupling the approximation of stationary states of giant basis eigenvalue problems with associated ionic dynamics, even for a basis other the plane-waves.

In the next paragraphs, I will discuss the basic CP equations of LDA on a plane-wave basis. To keep to the essentials I will write the expressions only for the Γ point of the Brillouin zone. For a complete discussion of the method, see Ref. [35]. As usual, the LDA equations take the form (for LDA Hamiltonian $\mathcal{H} = p^2/2m + V_{\text{eff}}$):

$$\mathcal{H}|\chi_i\rangle = \epsilon_i|\chi_i\rangle \tag{8}$$

where

$$|\chi_i\rangle = \sum_{\mathbf{G}} A^i_{\mathbf{G}}|\mathbf{G}\rangle, \tag{9}$$

where $|\mathbf{G}\rangle = 1/\sqrt{\Omega}\ \exp(i\mathbf{G}\cdot\mathbf{x})$, Ω is the cell volume, and $\mathbf{G}$ labels reciprocal lattice vectors (*a plane-wave basis restricts our studies to periodic systems*), so that the usual apparatus of reciprocal lattices is appropriate. The sum is cut off for $G = G_c$ large enough ("wavelength" small enough) that the smallest salient features in the problem are adequately described. An obvious advantage of this representation is that the kinetic energy operator is diagonal and therefore trivial. Matrix elements of V_{eff} are obtained by fast Fourier transforms, the existence of which makes the plane-wave approach tractable. The *problem* with Eq. (8) is that for systems large enough to interest us, the Hamiltonian matrix is too large to diagonalize with "classical" methods.

The key contribution of CP was to note that the diagonalization (Eq. 8) is unnecessary; it is adequate instead to consider the LDA expression for the total energy (a 'partial trace' over the occupied electronic subspace) and vary the χ_i:

$$E(\{\chi_i\}) = \sum_{i\ occ} \langle\chi_i|\mathcal{H}|\chi_i\rangle \tag{10}$$

where two important facts must be emphasized: (1) the sum is over the *occupied* subspace and (2) $\langle\chi_i|\chi_j\rangle = \delta_{ij}$. Thus, using Eq. (9), E can be viewed as a function of an extremely large number of parameters A^i_G ($n_{pw} \times n_e/2$) for n_{pw} the number of reciprocal lattice vectors used and n_e the number of electrons (double occupancy assumed). The idea is that if a set of mutually orthogonal $|\chi_i\rangle$ can be found, adequate in number to accomadate the electrons in the problem, and minimizing the functional (Eq. 10), then the E so obtained is the LDA ground state energy, to the extent that the basis is complete.

To perform the minimization, CP introduces a fictitious Lagrangian[3] which includes both the electronic and ionic degrees of freedom:

$$\mathcal{L} = \sum_i \mu/2\langle\dot{\chi_i}|\dot{\chi_i}\rangle + \sum_\alpha 1/2M_\alpha\dot{\mathbf{R}}^2_\alpha - E(\{\chi_i\},\{\mathbf{R}_\alpha\}). \tag{11}$$

In this equation, $E(\{\chi_i,\mathbf{R}_\alpha\})$ is the same as that given in Eq. (10) (the expectation value for the electronic energy, viewed as a functional of the orbitals χ_i), and the quadratic terms involving time derivatives (dots) are for the electrons (χ_i) and ions ($\mathbf{R}_\alpha$). Parameter μ is a fictitious mass assigned to the electron (it has nothing to do with the real mass, and is adjusted to make the calculation proceed efficiently). Note at this point that this method *does not* provide any information about electron dynamics in the usual quantum mechanical sense of time evolution. Rather it is just a trick to find the stationary states of the LDA Hamiltonian (approximate the occupied eigenstates from eigenvalue problem Eq. 8). Thus, the "dynamics" for the electrons has only the utility of helping to solve the eigenvalue problem, and in fact if the fictitious kinetic energy becomes significant compared to the physical ionic kinetic energy, the dynamics for the ions will be suspect. In the absence of the "fictitious electronic kinetic energy", this Lagrangian would just generate the Newton equations of motion for the ions $M_\alpha \ddot{\mathbf{R}}_\alpha = -\partial E / \partial \mathbf{R}_\alpha$, as one would expect. The additional term adds an extra equation however: $\mu|\ddot{\chi_i}\rangle = -\delta E/\delta\langle\chi_i| + \sum_k \Lambda_{ik}|\chi_k\rangle$. Here, Λ_{ik} is a matrix of Lagrange multiplers required to maintain orthogonality $\langle\chi_i|\chi_j\rangle = \delta_{ij}$. In practical methods the Λ_{ik} are obtained by compelling the eigenvectors $|\chi_i\rangle$ to be orthonormal at each time step, and computing Λ_{ik} from $\Lambda_{ik} = \langle k|\mathcal{H}|i\rangle - \mu\langle\dot{\chi_k}|\dot{\chi_i}\rangle$. Then the ionic and fictitious electronic "forces" are completely specified, and the determination of the stationary states can proceed. Note that there are effectively two time scales in the dynamics so generated: one is determined by the artificial "mass" μ of the electrons; the physically salient time scale is set by the ionic masses M_α. This method generates unreliable dynamics for the ions if significant energy is transferred from the ionic (physical) degrees of freedom to the fictitious electronic degrees of freedom. That this must happen for long times is apparent from the equipartition theorem (Eq. (11) is a quadratic form, and asymptotically energy will reach equipartition at least if the ionic coordinates are near an energy minimum). It develops that the rate of transfer from the ions to the unphysical electron kinetic energy depends critically on the energy gap (rapid transfer for small gap), which makes the CP method difficult to apply to metals. This is best discussed in Reference [36].

2.5. BEYOND THE LOCAL DENSITY APPROXIMATION

At the present time (1996), the LDA is the universal choice for *ab initio* calculations on amorphous systems. There are, however, well known problems with the approximation: (1) the optical gap is always poorly estimated (normally *underestimated*). This does not affect ground state properties like charge density, total energy and forces (and therefore dynamics), but it can be a serious headache for calculations of conduction states, as for example in the case of transport or optical properties. Moreover the gap is of particular interest for certain types of applications like photovoltaic device studies. While the so called "scissors" approximation is useful for the bulk (this amounts to just introducing an offset of conduction states to match experiment), this is not possible in cases where we do not already know the answer from experiment! (2) In strongly (electronically) inhomogeneous systems such as SiO_2, the basic assumption of weak spatial variation of the charge density is not well fulfilled, and the LDA has difficulty. (3) The LDA implicitly assumes that the system is paramagnetic; the local spin density approximation[37] (LSDA) (in which a separate "spin up" and "spin down" density functional is used) is useful for systems with unpaired spins, as for example a half filled state at the Fermi level. (4) A final example of less interest to the glass community is that weak bonds (as for example of fluctuating dipole type) are poorly described in LDA; and hydrogen bonding is also not very well described in the LDA.

Two general classes of attack on the problem can be identified. Several workers, but especially Perdew[38], have worked on the natural next step to the LDA: inclusion of effects proportional to the gradient of the charge density. Recent improvements along these lines are called "generalized gradient approximations" (GGA), and these seem to have led to significant improvements in SiO_2[39], and intermolecular binding in water is better described with GGA than in the LDA. In some ways the GGA's have been disappointing; on very precise measurements on molecules the results have been mixed. Overall, however, the GGA seems to be an improvement over the conventional LDA, and it is an area with much activity. In the general context of "patching up LDA", the "GW" approximation of Hedin[40] has been much applied to surface problems, particularly by Louie[41].

The other approach is to abandon the LDA altogether, and either develop entirely new exchange-correlation functionals[23], or abandon density functional theory for essentially "exact" calculations from the full many-body Hamiltonian. The most promising work appears to be the Quantum Monte Carlo (QMC) work of Mitas and coworkers. Such calculations allow a statistical sampling of the true many particle wave functions, and enable accuracy much better than LDA calculations. At the present time, it is a stretch to handle more than about 100 electrons. The increasing relevance of QMC to large systems is due in large measure to the introduction of pseudopotentials[42] into the scheme. This has allowed exceedingly accurate calculations on 20-atom clusters of Si[43] and C[44]. An indication of the salience of these methods arises from considering 20 atom C clusters[44] with carefully converged *ab initio* Hartree Fock calculations, LDA calculations, using several GGA approximations and QMC gave different results for the energies of C_{20} isomers, and different GGA's actually changed the energy ordering of some of the isomers[45]. The QMC calculations revealed that in C there are very subtle effects arising from electron correlations that have some structural implications even in a 20-atom C cluster: certainly one can expect that such effects exist in a-C as well, though it is unlikely that their inclusion will change our qualitative understanding of the material substantially.

In addition to molecular applications, QMC has been applied to a few solids, and gives excellent agreement on cohesive energies (LDA tends to overbind by as much as 20%); and also reproduced the band structure of the column IV materials very well (for the case of diamond, see Ref. [46]).

At the moment, force calculations have not been implemented in QMC, and it is still limited to systems too small to have direct relevance to amorphous systems, but it seems certain that within the next several years, with methodological developments and improvement in computer technology, accuracies at the level of 0.01 eV/atom will be attainable[47], and will find use in the glass community.

3. Linear system size scaling methods

3.1. THE NEED TO MODEL LARGE SYSTEMS

The common approach to model a glass or amorphous solid is to set up a supercell and impose periodic boundary conditions to eliminate surface artifacts. Of course this construction introduces a physically nonexistent periodicity which can nevertheless strongly influence the results. We can view this in different ways: Most properly we should admit to ourselves that the use of supercells and periodic boundary conditions *is* a calculation on a crystal with a large unit cell. From an electronic point of view then, Bloch's theorem applies, and quantities like the total energy and the forces involve quadratures in reciprocal space. *If it is the case that there is a significant dispersion of the bands, then it is likely that the cell is too small to use as a model for an amorphous material.* At a practical level this should be checked by computing the Hamiltonian (and overlap for a nonorthogonal local basis calculation) at several $\mathbf{k}$ values and checking that the total energy *and especially the forces* are converged to whatever tolerance is set[48]. At a more physical level, one can understand the effects of small cells as causing the formation of impurity bands. In many amorphous semiconductors (like a-Si) defects are really quite rare, occurring less than once per 1000 atoms. The best supercell calculations typically have a few to several *per cell* – there are many calculations that purport to describe a-Si with more than 10% defects. Because of both inter- and intracell interactions (because the defects tend to have similar electronic energies), the states on the defects mix, and this reduces the localization substantially. At its most extreme it is possible even for a specific defect to directly interact with its own image in neighboring cells. This problem is quite obvious when comparisons are made to experiments; the localization is always much higher (as measured by spin resonance experiments) in the real material than in computer models).

It is important to note that these effects extend well beyond inadequately localized electron states: Since the electronic eigenvectors are different, so is the density matrix and therefore the forces. Thus the structure itself, the vibrational modes, and anything else of physical importance is affected.

To begin the discussion of quantum “order N” methods (so called because the computational cost (memory and CPU) scales linearly with N, the number of atoms in the system), I discuss a method for extracting the density of electronic states from giant matrices. I limit the discussion to the orthogonal eigenvalue problem[49], though the ideas have recently been extended to the case of a non orthogonal basis[50].

Let H be a large, sparse, Hermitian matrix of dimension N. Ideally one would like the eigenvalue spectrum ϵ_i, where $H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$. We note that the information carried by the density of states is contained in any one single vector $|\xi\rangle$ in the family of vectors of the form

$$|\xi\rangle = N^{-1/2}\sum_{j=1}^{N} e^{i\phi_j}|\psi_j\rangle, \tag{12}$$

where ϕ_j specifies an arbitrary phase. Note that the expectation value of the DOS operator $\hat{\Delta}(E) = \delta(E - \hat{H})$ between any $|\xi\rangle$ gives the exact density of states; $\rho(E) = \langle\xi|\hat{\Delta}(E)|\xi\rangle$. The vectors $|\xi\rangle$ equally weigh all of the eigenvalues of the spectrum of H. For this reason we call such $|\xi\rangle$ *impartial vectors.* The Hamiltonian H has moments μ_n,

$$\mu_n = \int_{-\infty}^{\infty} dE E^n \rho(E) = \frac{1}{N}\mathrm{Tr}H^n. \tag{13}$$

We then see that an impartial vector also generates exact moments through its expectation value,

$$\mu_n = \langle\xi|H^n|\xi\rangle. \tag{14}$$

However, as we discuss below, the expectation value is an $O(N)$ operation, while taking the trace in Eq. 13 is not.

Skilling [51] noted the possibility of extracting moment data from the operation of sparse matrices on random vectors and derived useful error estimates for errors for integrals over $\rho(E)$. Silver and coworkers [52] used random vectors to generate moment data and used an orthogonal polynomial fit for the DOS of the 2D 4x4 Heisenberg model. Here we greatly extend the practical value of this earlier work and investigate its appropriateness for electronic structure applications by applying it to problems so large that they would otherwise be intractable with existing techniques. We should point out that Lanczos[53] understood most of this as early as 1956, and many workers[54, 55] have redeveloped ideas related to the work we present here. It is historically relevant to note that a very early moment expansion (for thermodynamic quantities related to the vibrational DOS) dates prior to the first World War[56]!

The first step of our technique is to show that approximate moments of ρ are readily obtained. Let $|x\rangle$ be an arbitrary random normalized vector in the space of H. Now consider the following sequence ν_k, where

$$\nu_k = \langle x|H^k|x\rangle \;=\; \sum_{lm} x_l^* x_m \;(H^k)_{lm}. \tag{15}$$

These objects are the moments of a nonnegative function $\rho_x(E)$ for any x as can be seen by inspecting Eq. 15 with x expressed in the energy representation. Now consider an average over an ensemble of RVs $|x\rangle$:

$$\overline{\nu_k} \;=\; \sum_{lm} \overline{x_l^* x_m}\;(H^k)_{lm} \rightarrow \mathrm{Tr}\; H^k \;=\; \mu_k, \tag{16}$$

where the last result is fulfilled for *any* sampling scheme (random or otherwise) which produces $\overline{x_l^* x_m} \rightarrow \delta_{lm}$, and the bar denotes ensemble average. Thus, a random process can lead, without any knowledge of the energy eigenvectors, to arbitrarily accurate estimates for the moments μ_k of the DOS. Some such processes are more efficient than others. A simple approach is to sample the components of $|x\rangle$ independently from the unit normal distribution then rescale to get $\langle x|x\rangle = 1$. In our first report of this method[49], we thought it necessary to average the DOS (instead of the moments). In fact we find that averaging the moments and using the averaged moments to obtain a DOS is adequate, and more efficient. In addition, an appealing aspect of this simple method is that for estimates of the DOS, the number of vectors $|x\rangle$ *decreases* with increasing system size.

The ν_k are easily computed, as observed by Skilling [51] and Silver *et al.* [52] for sparse H, since ν_k may be computed recursively. If we define $|y_k\rangle = H^k|x\rangle$, then $|y_{k+1}\rangle = H|y_k\rangle$, and $\nu_k = \langle x|y_k\rangle$. Thus, we may accumulate the ν_k by repeated operations of a sparse matrix on a vector. These calculations are $O(N)$.

A unique feature of our work, salient for computing integrals over the DOS, is to use special vectors selected to approximate $|\xi\rangle$, to produce improved moment data $\{\nu_k\}$ from H. We show elsewhere[49] that this dramatically improves the method for computing band energies, the Fermi level or any other quadratures involving ρ. To obtain these improved vectors, we construct a penalty function of a vector $|x\rangle$ subjecting it to three constraints (μ_0, μ_1 and μ_2),

$$\pi(|x\rangle) = (\langle x|x\rangle - \mu_0)^2 + (\langle x|H|x\rangle - \mu_1)^2 + (\langle x|HH|x\rangle - \mu_2)^2 \tag{17}$$

The exact moments μ_1 and μ_2 are both $O(N)$ calculable, and by normalization, μ_0=1. We minimize the function (Eq. 17) with a conjugate gradient (CG) method [57]. We find that it is always straightforward to generate $|x^*\rangle$ such that $\pi(|x^*\rangle) = 0$ from an initial random vector $|x\rangle$. Note that such $|x^*\rangle$ is 'closer' to an impartial vector $|\xi\rangle$ than an $|x\rangle$ merely chosen at random and normalized [51, 52].

The second key step in our technique is to transform the information contained in $|x^*\rangle$ into $\rho(E)$ through moment data (Eq. 15). As demonstrated by a variety of workers [58, 59, 60, 61], Maxent offers a very rapidly convergent approach to computing the density of states from its moments. Because of its information theoretic origin [62], Maxent introduces no artifacts stemming from *ad hoc* approximations. It is also manifestly nonnegative, a desirable feature for a spectral function. For numerical convenience, we scaled and shifted H so that the DOS has support only on (-1,1), and we used Tchebychev polynomials, T_n, instead of raw powers. It is these shifted and scaled units that are used in the figures of this paper. In practice, one can use low-order Maxent approximations to the DOS to obtain an approximate width, and modify H accordingly. Thus, no highly accurate guess is required *a priori* for the width. Given averaged moment data $\overline{\nu_k(x)}$, the Maxent reconstruction is $\rho_M(E) = \exp[\sum \lambda_n T_n(E)]$, where the Lagrange multipliers λ_n are determined by requiring the Maxent DOS reproduce the input moments $\{\overline{\nu_k(x)}\}$. See Turek [60] for a stable algorithm to solve the Maxent moment problem, and for details on the use of orthogonal polynomials see Ref. [51]. The ease of computing integrals over the DOS is also useful for other order N methods[63] which do not provide DOS (and therefore Fermi level) information. For examples of the spectral resolution obtainable with these methods, see References[64], [65]. Codes to implement these calculations are available from the author[66].

3.3. APPLICATION: BAND TAILING IN AMORPHOUS DIAMOND

I have chosen to discuss one detailed application in this paper involving a large system (order N methods) and electronic structure issues[67]. One of the central issues of the physics of glassy and amorphous solids is the nature of the band tails in the electronic density of states (DOS). Particular issues include: (1) What is the origin of the ubiquitous exponential shape of the tails seen in photoemission and less directly in optical absorption measurements[68] and (2) How does the spatial character of the electronic eigenstates change from the highly local midgap states to the extended states interior to the valence or conduction bandsΓ The nature of the electronic states for electron energies ranging between midgap (localized) to valence or conduction (extended) is of obvious interest to the theory of doping and transport. The tools required to address such questions in an unambiguous way are (1) *very large and realistic structural models of a representative amorphous system.* Small models can give a good account only of the the most highly localized midgap states, and necessarily fail in describing the spatial structure of the states as the volume of the state exceeds the volume of the supercell. Tantalizing hints of the nature of band tailing have been observed in earlier work on small supercells[69] and with elegant calculations using Bethe lattice techniques[10], which cannot provide a useful description of the spatial structure of the disorder-influenced electronic states. The structural model of this paper is a 4096-atom cubic supercell model of a-diamond (a-D) provided by Djordjevic, Thorpe and Wooten.[70] We note that a-D is a hypothetical, entirely fourfold material at a density of 3.52 gm/cm^3 as crystalline diamond, but with topological (primarily bond angle) disorder. It is probably related to tetrahedral amorphous carbon (ta-C), which, however has a lower density (3.0 gm/cm^3) and contains about 15% sp^2 sites[71]. Column IV amorphous semiconductors a-Ge and a-Si are the materials most resembling a-D, with their large proclivity for sp^3 bonding (good quality unhydrogenated a-Si is believed to have less than 0.1% non-sp^3 sites). That the cell of Ref. [70] is a structurally credible model of amorphous diamond can be inferred from our LDA relaxations of smaller versions (216 and 512 atom models) constructed in an analogous fashion with the Wooten-Weaire-Winer (WWW) method[72]. We found that these smaller supercells of a-D were practically unchanged upon relaxation. We reported on this in more detail elsewhere[73]. At present, several thousand atom structural models are unattainable from *ab initio* molecular dynamics simulations. The second tool needed is: (2) *electronic structure methods able to cope with the large Hamiltonian matrices from which spectral information is required.* We use recently developed maximum entropy[62] spectral methods[49, 65] to handle the state density calculations and a shifted Lanczos[74] scheme to compute the electronic states of interest from the sparse 16384 × 16384 Hamiltonian matrix. We use a block Lanczos method[75] and sparse matrix techniques to implement these calculations. We make the simplest reasonable choice of an electronic Hamiltonian; the orthogonal tight-binding Hamiltonian of Xu et al[14]. For the *spectral* calculations we report here this Hamiltonian is a reasonable choice. Its reliability is also in little doubt for an entirely four-coordinated matrix as we study here. We concentrate on the valence band tail in this paper since the basis of the Xu et al. Hamiltonian is minimal (one s and three p orbitals per site).

A variety of experiments on amorphous systems show the density of band tail states falling exponentially into the bandgap[76]. It is clear that both structural and thermal disorder contribute to the tail[69]: this work focuses entirely on the structural origins of exponential tailing. Where structural broadening is concerned, an early argument of Halperin and Lax, [77] led to a DOS $N(E) \propto \exp(-\gamma|E|^{1/2})$ in three dimensions, and later Soukoulis *et al.* (1984)[78] modified the theory with scaling localization arguments and obtained the correct exponential form of the DOS. As a complement to this work, we give a simple argument below which also leads to exponential tails. The electronic DOS of our amorphous diamond model is computed with the maximum entropy method[49] and illustrated in Fig. 1.

Compactly stated, random vectors and an averaging scheme are used to obtain up to 100 moments of the density of states of the sparse Hamiltonian matrix, and maximum entropy techniques are used to reconstruct the DOS from the moments. Care was taken to properly converge the results with respect to both the number of moments and random vectors[49]. For an illustration of the spectral resolution this method affords, see Ref.[65] and [64]. In Fig. 2a we show the valence band edge region for diamond in a 4096 atom cell and the tails from the Djordjevic cell. The crystalline diamond cell has a defect-free gap with sharp band edge, while the amorphous diamond model has extended band tailing at both valence and conduction bands, as well as a few defect states in the middle of the bandgap. Different numbers of moments and random vectors are used to compute DOS. Fig. 2b shows that our result of 80 moments and 50 vectors is well converged. These parameters, particularly the number of random vectors selected, is very conservative.

A semi-log plot (See Phys. Rev. B **54** 10284, 1996), reveals that the band tail falls exponentially , which agrees with the experimental observation. The tail decay parameter E_0 [such that the valence DOS $\propto \exp(-E/E_0)$] is about 180 meV (versus approximately 60 meV seen in photoemission studies on a-Si)[76]. We also find it useful to present a simple heuristic argument for the origin of structural exponential tailing for the valence edge, based upon the following assumptions. First, as suggested by Bethe lattice calculations[10], we view band tailing as originating in bond angle distortions from the tetrahedral angle θ_T; and we further assume that an energy deviation from the diamond valence edge value can be assigned associated with these distortions. This effectively assumes that the states in question are substantially localized. Second, we have observed that the distribution of the cosine of bond angles θ in the cell is very well approximated with a normal distribution $p(\xi) = \exp[-(\xi - \xi_t)^2/2\sigma^2]/(2\pi\sigma^2)^{1/2}$ with $\xi = \cos(\theta)$, $\xi_t = \cos(109.01^\circ)$ (the mean bond angle is near θ_T, as expected), and $\sigma = 0.149$ (corresponding to a dispersion in θ of about 9.0°). This bond angle distribution was generated by the WWW method, and is seen in the smaller 216- and 512- models as well, and as we pointed out, *it is preserved under an LDA relaxation in 216 and 512 atom models* lending

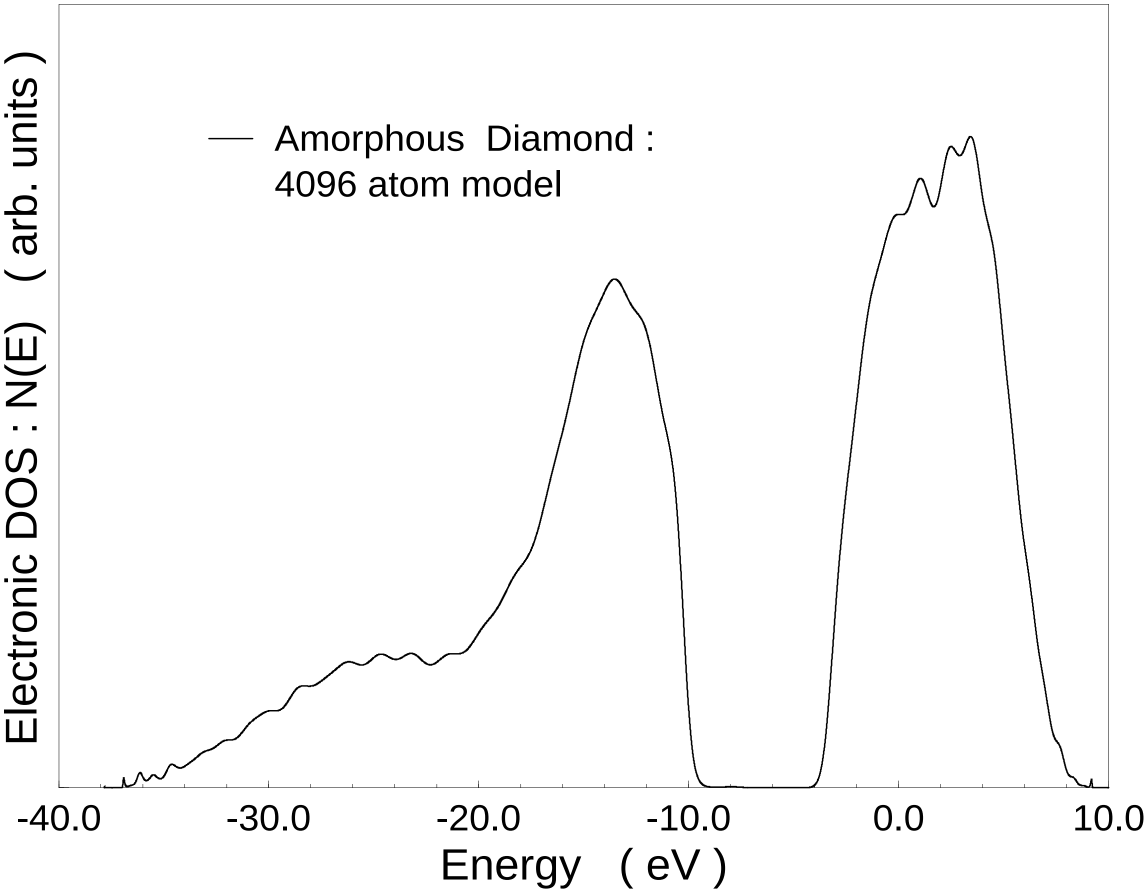

Figure 1. Total electronic density of states (DOS) of amorphous diamond: 80 moments and 50 random vectors were used.

some credence to the view that the normally distributed cosines are realistic at least for dominantly four-coordinated systems. To investigate this further, we would like to consider bond angle distributions in supercell models generated entirely from *ab initio* methods, but there are two problems with this: (1) the statistics are poor because of the small cell size and (2) the unphysically large number of defects obtained in virtually all *ab initio*

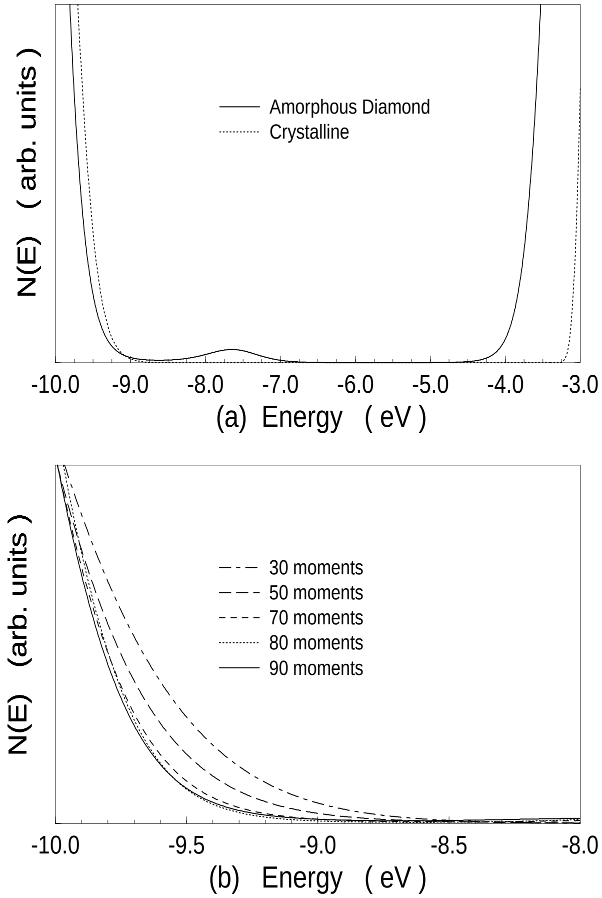

Figure 2. (a) Electronic DOS in the bandgap region. The solid curve depicts a-D; dotted curve is crystalline diamond. (b) Results with different numbers of moments. Convergence of the maximum entropy reconstruction is obtained with 80 moments and 50 vectors.

simulations introduces a complicating factor in interpreting the resulting distributions. With the assumption of normally distributed cosines, we take the crystalline valence band edge to be at energy λ_V. As $\lambda(\xi)$ is presumably a minimum for $\xi_T = \cos(\theta_T) \approx \xi_t$, this function can be approximated for small distortions as $\lambda = \lambda_V + K(\xi - \xi_t)^2$, where K is a positive constant[79]. As the probability density function (PDF) of $\xi = \cos\theta$ is normal, one can easily write the PDF for λ, the highest valence band eigenvalue as broadened by the structural disorder of this model, by using the usual rule for changing variables in a PDF. One obtains: $N(\lambda) \propto \exp\left(-|\gamma(\lambda - \lambda_V)|\right)$, where $\gamma = (2\,\sigma^2\,K)^{-1}$. An essentially identical argument can be stated for the conduction tail. We note that in this simple picture, *any* mechanism causing approximately Gaussian bond angle disorder leads to exponential tails. Consider a very simplified model for the network dynamics, and assume the lattice is in thermal equilibrium at finite temperature T. In a valence force field model[80], the energy associated with bond bending involves a term of the form $U = \epsilon_0[\delta\cos(\theta)]^2$, where $\delta\cos(\theta)$ is the deviation of the angle between adjacent bonds from $\cos(\theta_T)$. Parameter ϵ_0 may be inferred from Ref. [80] for a variety of materials. If one neglects other distortions, comparison to the canonical distribution function suggests that thermal disorder leads to normally distributed cosines (with the width of the distribution $\sigma^2(T) \propto T$). The resulting linear dependence in the exponential "tail width" is clearly seen in experiments for the conduction tail in Ref. [76] (for a-Si), and less obviously for the valence tailing, which seems to be mostly structural in origin.

To show the nature of these band tail states, we apply a shifted Lanczos method[74] to probe the midgap and valence tail energy region. We computed about 30 eigenstates in the valence band tail. The localization is characterized by the inverse participation ratio (IPR) defined as: $I(\psi_j) = N\sum_{i=1}^{N} {a_i^j}^4 / \sum_{i=1}^{N} {a_i^j}^2$ where $\psi_j = \sum_{i=1}^{N} a_i^j \phi_i$ is the j^{th} eigenvector and $\{\phi_i\}$ is the (tight-binding) orthogonal basis and $N = 16384$, the number of basis functions. Note that $I = 1$ for completely uniform extended states and $I = N$ for a state completely localized on a single orbital: results are presented in Fig.3.

The first several defect states in the middle of the gap ($E \approx -8eV$) are strongly localized. As the energy approaches the interior of the valence band, (from about $-9eV$ to about $-10eV$), the degree of localization substantially decreases. This localized to extended transition is more clearly shown in Fig. 4. Atoms are assigned different grey scale renderings (darker more charge localization) according to their contribution to the eigenvectors. Atoms making little contribution (where $< 0.05\%$ of the "charge" is located) are omitted in Figure 4. The origin of the midgap defect states is found to be an atom that has very large bond angle distortion ($\Delta\theta \approx 20°$).

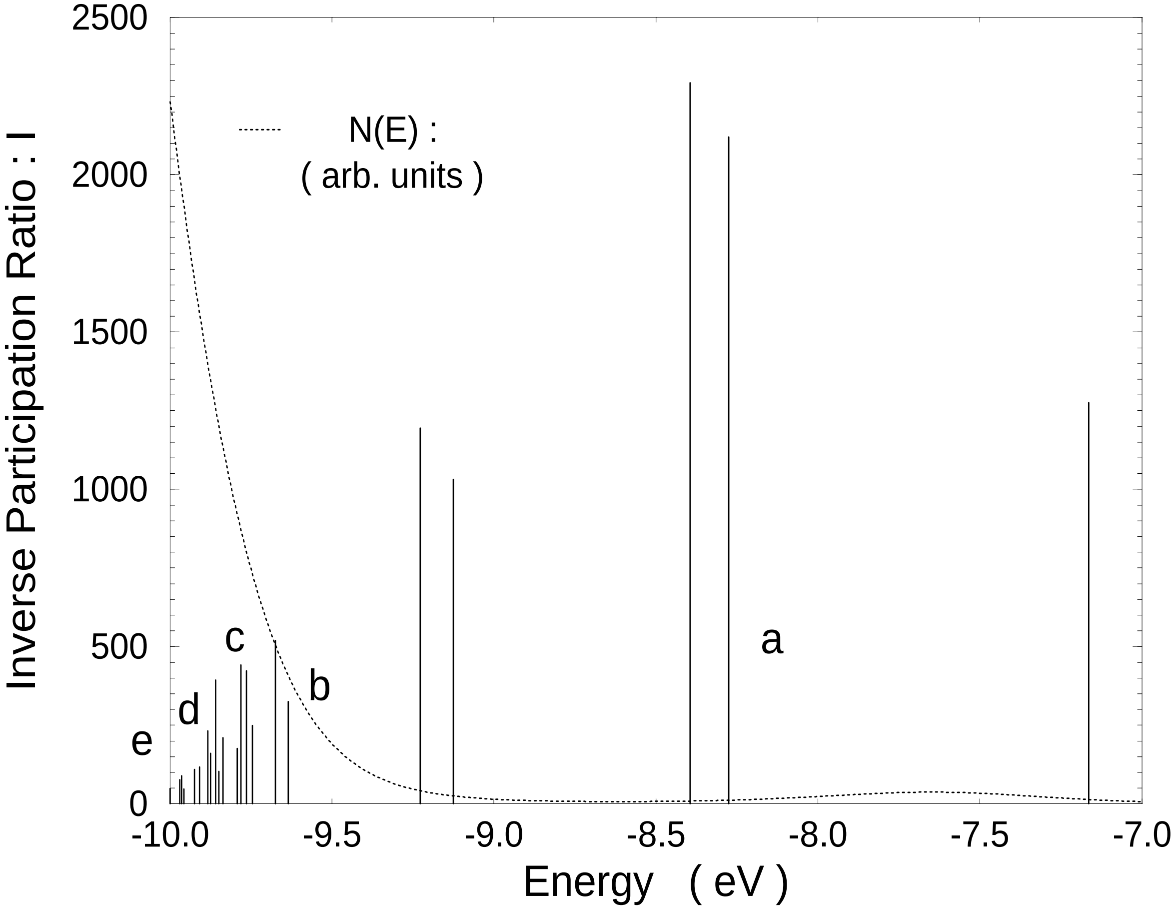

Figure 3. DOS and localization as measured by the inverse participation ratio in the valence band tail region. The letters refer to Fig. 4.

Such states are strongly localized on the defect core and its nearest neighbors. As we expect, such large angle distortions are rare in the model, so only a few (3 of 16384) midgap states are found. States deeper into the band tail do not just localize on several atoms, but tend to have weight on certain clusters of atoms. The deeper the state is inside the band, the larger of the size of cluster, which implies smaller IPR. There is an in-

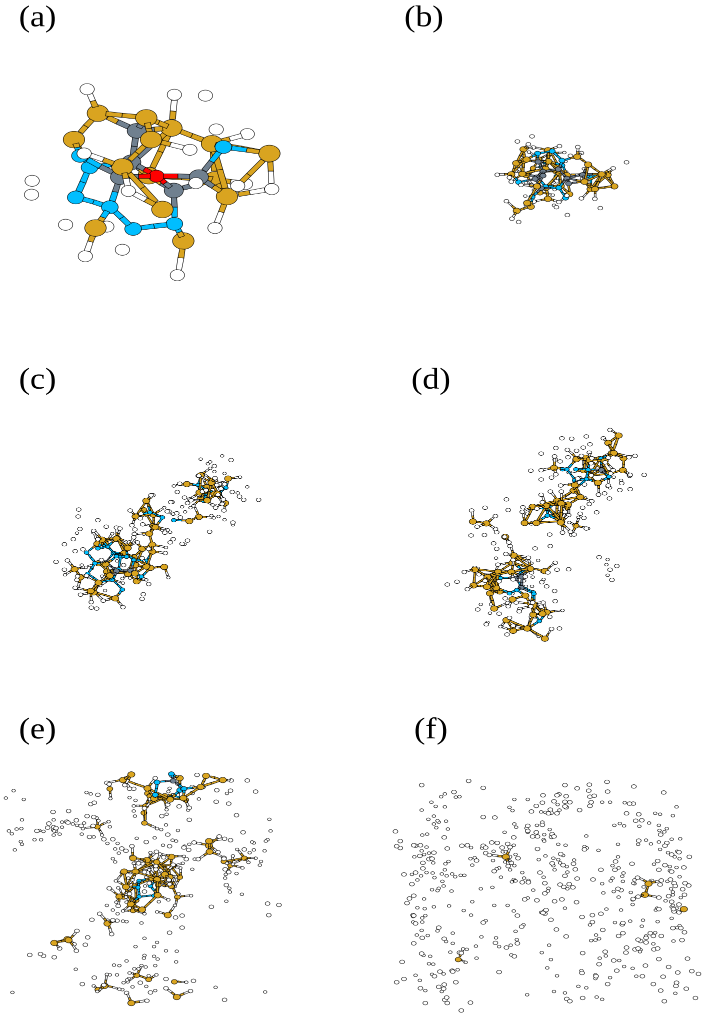

Figure 4. Spatial character of the local to extended transition. I is the inverse participation ratio (see text). (a)$E = -8.27eV$: highly localized midgap state (I=2120); (b)$E = -9.63eV$: less compact cluster (I=326); (c)$E = -9.84eV$: larger cluster (I=210); (d)$E = -9.92eV$: weight on two separated clusters (I=110); (e)$E = -10.0eV$: nearly extended state (I=49); (f)$E = -11.0eV$: extended valence state (I=5).

Note the puppet strings of the deity (postscript curiosity).

teresting pattern, when the size of the cluster increases to certain point, the localized states start to "bifurcate" into two smaller spatially separated pieces (compare Fig. 4c and Fig. 4d). As we have pointed out elsewhere[81], using the simple language of perturbation theory, it is natural to see this as a "resonant phenomenon" in the sense that electronic states can spatially mix "energetically similar" parts of the network that are well separated in the supercell because of "small energy denominators" . We have seen a very similar resonance effect on vibrational eigenstates in glassy $\mathrm{GeSe_2}$[82]. As one progresses deeply into the valence tail, the fraction of the network associated with the given energy increases until the states become fully extended; for E close to $-10eV$, there is no clear pattern of clustering and states become quite extended.

3.4. FORCE CALCULATIONS

A more challenging problem is to extract *local* properties in an order N fashion. This includes *forces*, which are of course essential to any MD simulation. Here we outline the main ingredients (see Ref. [63] for a very complete discussion), which are (i) a new band structure energy functional which, when freely minimized with no orthogonalization constraints, yields the exact ground state energy and a set of orthonormal states defining the ground state subspace, and (ii) description of the system in terms of localized, Wannier-like functions, that are truncated beyond a certain cutoff radius R_c. The unconstrained energy functional has the form

$$\tilde{E} = 2 \sum_{i,j=1}^{N_e} H_{ji}(2\delta_{ij} - S_{ij}), \tag{18}$$

where $S_{ij} = \langle \chi_i | \chi_j \rangle$ and $H_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle$ are the overlap and Hamiltonian matrix elements between occupied orbitals $\{|\chi_i\rangle\}$ $(i = 1, ..., N_e)$ and $2N_e$ is the number of electrons. The set of functions defining the ground state is the one that minimizes the functional $\tilde{E}$. This is a key point: the χ_i are *not necessarily eigenvectors*; rather, they are just a set of orthonormal vectors spanning the occupied subspace with no unoccupied component. As the χ_i form an orthonormal set, the transformation connecting the χ_i to the eigenvectors is *unitary.* Therefore *all trace quantities (the band energy, the force, etc.)* are given as well by the χ_i representation as the eigenvectors. The χ_i are easier to obtain, and also allow the freedom of constructing them to be spatially local in insulators, which is of critical importance from a computational point of view. In particular, one of the possible equivalent sets of functions is a set of localized wave functions (LWF's), centered at different positions, similar to the Wannier functions for crystals. In the Order-N method of Ordejón *et al.* these LWF's are truncated beyond a cutoff radius R_c from the center of the LWF. When this is done, all the operations necessary to compute and minimize the energy functional $\tilde{E}$ scale linearly with the size of the system, since for each LWF $|\chi_i\rangle$ only the matrix elements H_{ji} and S_{ij} with orbitals $|\chi_j\rangle$ inside the radius R_c must be calculated (a number that is independent of the system size). It can also be shown that, once the LWF's have been obtained, the forces on *all* the atoms can also be obtained in O(N) operations.

3.5. NON VARIATIONAL (PROJECTION) METHODS

As the preceding discussion reveals, a spatially local representation of electronic states is very desirable, enabling us to partition space into regions involving the overlap of a finite number of Wannier-like functions and accurately compute the electronic structure order N. One can obtain these orbitals by making an initial (local) guess and performing the minimization described above. This is challenging in an arbitrary bonding environment. Thus, we have constructed Tchebychev polynomial approximations (after scaling and shifting H so that its spectrum lies on [-1,1]) of the projection (density) operator[83, 84]:

$$\hat{\rho} = \lim_{\beta\to\infty} \left(1 + \exp[\beta(\hat{H} - \mu)]\right)^{-1} \approx \sum_{l=0}^{M} \gamma_l(\beta, \mu)\ T_l(\hat{H}) \qquad (19)$$

where the limit really only implies that β should be large enough that $\hat{\rho}$ annihilates unoccupied states, and multiplies occupied states by unity, to a suitable degree of convergence; μ is the chemical potential specifying the demarcation between occupied and unoccupied states. We employ Tchebychev polynomials because of their property of rapid uniform pointwise convergence to the Fermi-Dirac operator[83]. The number of terms (M) required depends upon the gap (which determines β), and the total bandwidth of the spectrum. The γ_l are easy to determine from the form of the Fermi-Dirac distribution[57]. In a typical practical calculation (as for example c-Si or c-GaAs) $M \approx 50$ has been found to be adequate. A larger gap requires a smaller β (which is easier to approximate since the projection operator is smoother for energies near μ). Thus, *as usual*, insulators are easier to handle than metals[85]. As one might expect, if this operator is applied to a spatially local vector, this locality is substantially preserved, *and the resulting state is entirely constructed from eigenvectors* $|\psi\rangle$ *in the occupied subspace.* These projected states are suitably designated as "generalized Wannier functions", and what is best, these calculations can be carried out without any minimization: just a single application of $\hat{\rho}$ on an arbitrary vector, which is O(N). We[86] have adapted the method to making the initial guesses as a complement to the Ordejón *et al.* order N scheme.

The use of a projector leads to a very simple approach to force and dynamics calculations. Note that Equation 19 is a general operator equation. In an arbitrary representation $|\omega\rangle$, the density operator becomes the density matrix, and it is straightforward to compute the band energy

$$E = \sum_{\omega\nu} \langle\omega|\hat{\rho}|\nu\rangle\langle\nu|\hat{H}|\omega\rangle \tag{20}$$

band structure forces

$$\mathbf{F}_{\alpha} \;=\; -\sum_{\omega\nu} \langle\omega|\hat{\rho}|\nu\rangle\langle\nu|\partial\hat{H}/\partial\mathbf{R}_{\alpha}|\omega\rangle. \tag{21}$$

and anything else related to the occupied subspace. In the foregoing equations, we may directly compute

$$\langle\omega|\hat{\rho}|\nu\rangle \approx \sum_{l=0}^{M} \gamma_l(\beta,\mu)\ \langle\omega|T_l(\hat{H})|\nu\rangle, \tag{22}$$

which is O(N) since (1) use of the Tchebychev recurrence relation avoids computation of matrix powers and (2) for real-space localized orbitals $|\omega\rangle$ and $|\nu\rangle$ sufficiently separated, $\rho_{\omega\nu} = 0$ for an insulator, (thus, such matrix elements need not be computed) a result following again from Kohn's[2] work. Recently, Goedecker[84] has implemented orthogonal tight-binding MD with essentially these approximations, and Stephan and Drabold[86] have generalized to *ab initio* MD with a local basis by including the effects of overlap.

3.6. PHONONS FROM ELECTRONIC STRUCTURE WITH LINEAR SCALING

In this section I point out that vibrational spectra may also be acquired in an order-N fashion[64]. The approach is based upon the finite differences dynamical matrix approach. The dynamical matrix $D_{\alpha I,\beta J}$, defined as $D_{\alpha I,\beta J} = (M_I M_J)^{-1/2}\partial^2 E/\partial u_{\alpha I}\partial u_{\beta J}$, where E is the total energy of the system, α and β are cartesian coordinates on atoms I and J, respectively, and the M's are ionic masses, is computed by finite differences: atom I is displaced an amount $\Delta x_{\alpha I}$ in the α direction, and the forces on all the atoms $\mathbf{F}_{\beta J}$ are computed. Then, $D_{\alpha I,\beta J} \approx (M_I M_J)^{-1/2}\mathbf{F}_{\beta J}/\Delta x_{\alpha I}$, since the force on an atom is the derivative of the total energy with respect to the displacement of that atom: $\mathbf{F}_{\beta J} = -\partial E/\partial x_{\beta J}$. We will assume that at the beginning of the computation we have solved the electronic problem for the system in equilibrium, in which all the atoms experience a zero force. We have therefore minimized the functional $\tilde{E}$ and obtained the localized electronic wave functions $\{\chi_j^0\}$ and the total energy E^0. During the process of computing the dynamical matrix, when atom I is displaced, we must minimize the electronic energy again, and find the new optimized localized functions $\{\chi_j^I\}$. At this point, we introduce the first basic approximation of our method: since the functions $\{\chi_j^I\}$ are localized, only those in the neighborhood of atom I will differ significantly from the solutions of the equilibrium system $\{\chi_j^0\}$. Therefore we can, as an approximation, optimize only those functions χ_j which are located close enough to the atom that is moving, leaving all the rest of the functions unchanged. The criterion used in this work is to allow variations in only those wave functions which include the atom that is being displaced. We denote this set of functions as $\mathcal{S}_I \equiv \{\chi_j \mid |\mathbf{R}_j - \mathbf{R}_I| < R_c\}$, where $\mathbf{R}_j$ is the center of χ_j, $\mathbf{R}_I$ is the position of atom I and R_c is the cutoff radius of the LWF's.

In order to obtain the optimized set of wave functions $\mathcal{S}_I$, we must minimize the energy functional $\tilde{E}$, defined in Eq. (18), with respect to the functions $\chi_j \in \mathcal{S}_I$. This is therefore a *restricted energy minimization*, since the functions that do not belong to set $\mathcal{S}_I$ are not allowed to change. During the minimization, there is a majority of terms in Eq. (18) that are constant: those involving matrix elements between functions χ_i and $\chi_j \notin \mathcal{S}_I$. It is convenient to separate those terms from the ones that do vary in the energy functional:

$$\begin{aligned} \tilde{E} &= 2 \sum_{i \text{ or } j \in \mathcal{S}_I} H_{ji}(2\delta_{ij} - S_{ij}) + 2 \sum_{i,j \notin \mathcal{S}_I} H_{ji}(2\delta_{ij} - S_{ij}) \\ &= \tilde{E}_1^I + \tilde{E}_2^I \end{aligned} \tag{23}$$

so that $\tilde{E}_2^I$ is constant during the minimization, and does not need to be computed. Therefore, the functions $\chi_j \in \mathcal{S}_I$ are obtaining minimizing the 'local' functional $\tilde{E}_1^I$. This operation scales as O(1), i.e., does not depend on the size of the system. This is easy to see, since if the system size is increased the number of functions included in the set $\mathcal{S}_I$ will not increase, provided that the system is large enough. Therefore, the solution of the electronic problem for the $3N$ atomic displacements (one per atom per direction in space) takes an O(N) effort. For each atomic displacement, once the electronic wave functions have been obtained in O(1) operations, we need to compute the forces on all the atoms in the system. This would be an O(N^2) task, since for each of the $3N$ atomic displacements we must obtain N forces. Here we introduce the second approximation of our method: only the forces on atoms closer than a certain cutoff R_f from the displaced atom are computed, the rest of the forces being set to zero. This approximation takes into account the fact that the forces on each atom depend ony on its local environment, and not on the details of the structure in distant regions. This also reflects the fact that the dynamical matrix elements between distant atoms decreases rapidly with distance. Our approximation can therefore be put in terms of imposing a cutoff on the dynamical matrix:

$$D_{\alpha I,\beta J} = 0 \quad \text{if} \quad |\mathbf{R}_I - \mathbf{R}_J| > R_f \tag{24}$$

so that the resulting matrix is sparse. Its calculation and storage are both O(N). With the dynamical matrix in hand one can exactly diagonalize D for small systems or use the Maxent spectral technique[49, 65] for large systems. In addition, the shifted Lanczos can be used for computing a limited number of vibrational eigenvectors in a user specified energy range[74]. Of course this method also works for empirical potentials in which case the germain approximations are that D have finite range and one of the spectral techniques described in this paper.

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