

Conventional electronic-structure theory of solids, clusters and molecules proceeds by first specifying the spatial coordinates of all atomic species involved, and then calculating the ensuing energy levels and wavefunctions:

$$\text{Atomic configuration} \rightarrow \text{Electronic structure} \quad (1)$$

We are interested in the counterpart to this direct approach: the 'inverse approach' of finding the atomic configuration that produces a prescribed electronic structure:

$$\text{Electronic structure} \rightarrow \text{Atomic configuration} \quad (2)$$

In the context of optical properties, such a method would provide answers to questions like "For a given superlattice orientation, what is the layer sequence that has the maximum bandgap (or a pre-assigned bandgap, say 2 eV)?"<sup>3</sup> In the context of transport properties, one could ask: "What is the crystal structure whose band structure maximizes Auger carrier multiplication?"<sup>4</sup> Similar 'inverse problems' can be addressed in the context of vibrational and photonic properties, as well as for molecules and low-dimensional systems.

We describe here a solution to the 'inverse band-structure problem' based on a direct exploration of the space of atomic configurations in search of the configuration possessing given electronic properties. The formidable complexity of this problem is best illustrated by an example. Consider a pseudo-binary substitutional alloy  $A_{1-x}B_xC$  of composition  $x$ , described by a unit cell of  $2N$  lattice sites, such that each of the  $N$  cation sites is occupied by an A atom or a B atom. The number of possible atomic configurations is  $N_{\text{config}} = N! / ((N-x)! x!)$ . For instance, for  $x = 0.25$  and  $2N = 128$ ,  $N_{\text{config}} \approx 10^{14}$ . Each configuration has, in principle, a different electronic structure, and therefore different electronic and optical properties. How many atomic configurations ( $N_{\text{search}}$ ) is it necessary to explore in order to find the configuration that has the target electronic properties? Clearly, if this approach is to be successful  $N_{\text{search}}$  should be small compared to  $N_{\text{config}}$ . We search the configuration space using a simulated-annealing algorithm that is able to 'learn the system' relatively quickly ( $N_{\text{search}} \approx 10^4$ ) by retain-

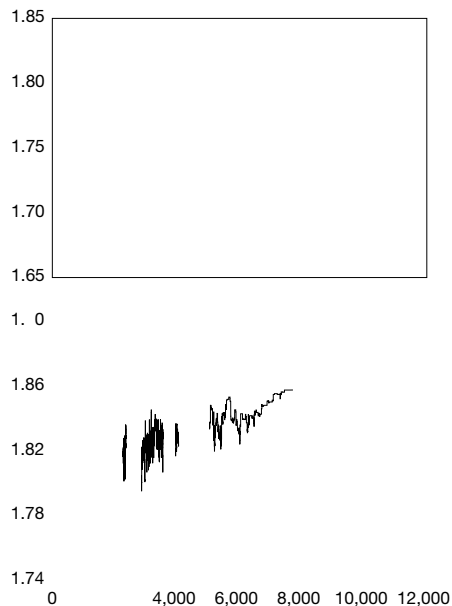
ing only those configurations that are conducive to the target electronic structure. Coupled with a fast, "Order  $N$ " solution of the Schrödinger equation, this method allows us to determine the target configuration of systems containing a few hundred atoms.

We consider substitutional systems described by an underlying lattice structure of  $N$  sites. An atomic configuration  $\sigma$  is defined as a set of  $N$  'occupation variables'  $\{S_1, S_2, \dots, S_N\}$ , where  $S$  denotes the identity of the atom located at lattice site  $i$ . The configuration variables  $\{S\}$  can be restricted to describe a particular experimental growth sequence, for example an  $A B A B \dots$  superlattice (where  $n_A, n_B$  denote the number of monolayers) oriented in the  $[001]$  direction. We then consider a set of electronic-structure properties  $P_\alpha(\sigma)$ , defined for every configuration  $\sigma$ , and the corresponding target properties  $P_\alpha^{\text{target}}$ . The subscript  $\alpha$  identifies specific properties, such as bandgaps, effective masses or oscillator strengths. The  $N$ -variable object function

$$O(\sigma) = \sum_{\alpha} \omega_{\alpha} |P_{\alpha}(\sigma) - P_{\alpha}^{\text{target}}|, \quad (3)$$

where  $\omega_{\alpha}$  is the weight assigned to the property  $P_{\alpha}$ , describes the 'distance' between the electronic structure of the configuration  $\sigma$  and the target electronic structure. This function  $O(\sigma)$  is minimized by varying the configuration variables  $\sigma = \{S_1, S_2, \dots, S_N\}$ , and calculating at each step  $P_{\alpha}(\sigma)$  from electronic-structure theory. This approach requires a fast-learning method of sampling the configuration space, and a numerically efficient yet physically accurate method of calculating the electronic structure of a given atomic configuration. Here we describe these methods.

(1)  $E_i, a, f, a, a$ . The simulated-annealing technique is an efficient algorithm for finding the global minimum of a multi-variable, multi-valley function. Given an atomic configuration  $\sigma$ , a trial configuration  $\sigma_{\text{trial}}$  is generated by elementary Monte Carlo moves, such as changing the identity of one atom, or swapping the positions of two atoms of different types. The trial configuration  $\sigma_{\text{trial}}$  is accepted with a probability distribution



$(\Delta O) = \min[1, \exp(-\Delta O/T)]$  where  $\Delta O = O(\sigma_{\text{trial}}) - O(\sigma)$  and  $T$  is a fictitious temperature parameter. By slowly decreasing the temperature to zero, the system is allowed to settle into the configuration that minimizes the object function  $O$ . We use an exponential temperature profile  $T = T_0 \exp(-i/\tau)$ , where  $T_0$  is the initial temperature and  $\tau$  is the temperature decay rate. Here  $i$  is the index of the simulated-annealing steps; each simulated-annealing step includes several elementary moves. The exponential temperature profile allows us to reduce the acceptance ratio in a nearly linear fashion. If the annealing process is too fast the system can become trapped in a local-minimum configuration. We can detect and avoid local minima by changing the initial configuration and/or the temperature profile.

(2)  $E_{\text{total}} = \sum_{i=1}^{N_{\text{at}}} \epsilon_i(a_i) + \sum_{i,j=1}^{N_{\text{at}}} V_{ij}(a_i, a_j)$ . This is done in three steps:

First, atomic relaxations: For each elementary Monte Carlo move the system is relaxed into the local energy minimum corresponding to the selected configuration (that is, without interchange of atoms). This task is accomplished using a valence-force-field method<sup>5</sup> whose parameters are fitted to a set of total-energy calculations for various configurations. The outputs are the equilibrium atomic positions  $\{a_i, i = 1 \dots N_{\text{at}}\}$  of the selected configuration.

Second, realistic hamiltonian: it is well known<sup>6</sup> that the conventional first-principle description of optical properties (the local-density approximation (LDA) to density-functional theory) produces systematic errors in the bandgap, a quantity that we are interested in here. We thus do not use the LDA approach. Instead, the electronic structure of each configuration is described by a semi-empirical pseudopotential hamiltonian:

$$H = -\frac{\hbar^2}{2} \nabla^2 +$$

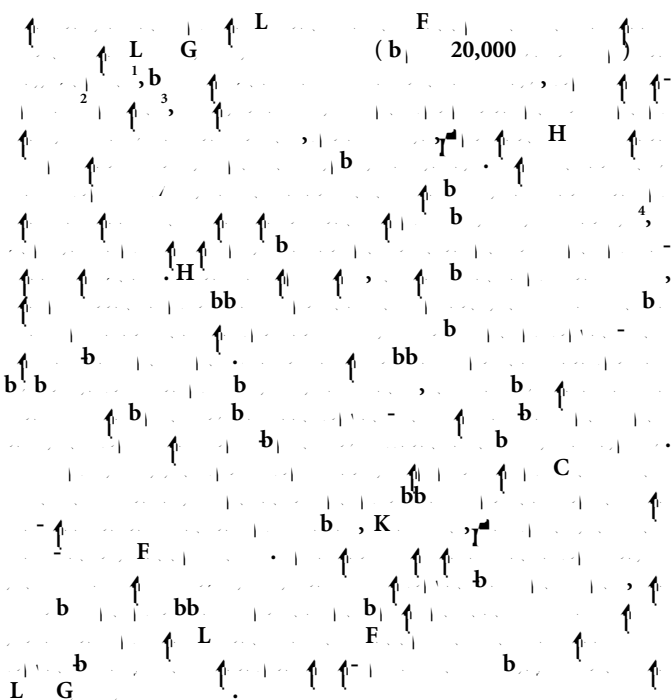
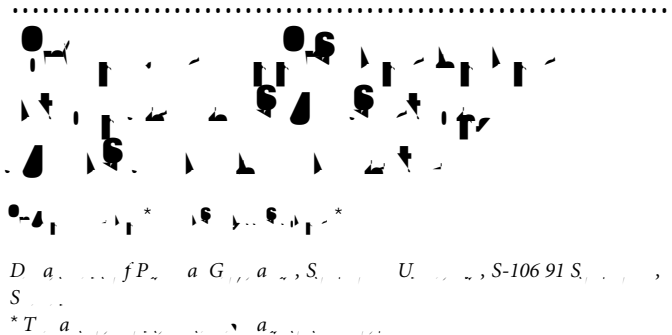
The first 'inverse problem' we consider is finding the configuration of AI

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The glaciological factors controlling the location of thermal zones (surface temperature, ice thickness, geothermal flux, strain heating) under ice sheets are well understood<sup>5</sup>, but because of the absence of direct subglacial palaeotemperature records, the actual basal thermal conditions under the Fennoscandian ice sheet (FIS) and Laurentide ice sheet (LIS) have remained elusive. Wide zones of subglacial till (glacially transported sediments) deformation have been invoked in modelling experiments predicting low ice-sheet profiles<sup>3</sup>, but without data on the phase state (frozen or thawed) of the sediments in deformable bed areas under glacial conditions, the validity of these models has been difficult to verify. The problem is that the rheology of subglacial till is extremely sensitive to the phase state of the interstitial water; frozen subglacial till is much stronger than ice, whereas thawed till under high water pressures can be deformed by overriding ice<sup>6</sup>. We focus here on the landform record

interpreted to result from the phase-state control on soil strength (and thereby landform-building processes) and perform an inver-