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Na[illegible] R[illegible] E[illegible] La[illegible], G[illegible], C[illegible] 80401, USA

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

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

We are interested in the counterpart to this direct approach: the `inverse approach' of ®nding the atomic con®guration that produces a prescribed electronic structure:

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

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)?''[3]. In the context of transport properties, one could ask: ``What is the crystal structure whose band structure maximizes Auger carrier multiplication?''[4]. Similar `inverse problems' can be addressed in the context of vibrational and photonic properties, as well as for molecules and low-dimensional systems.

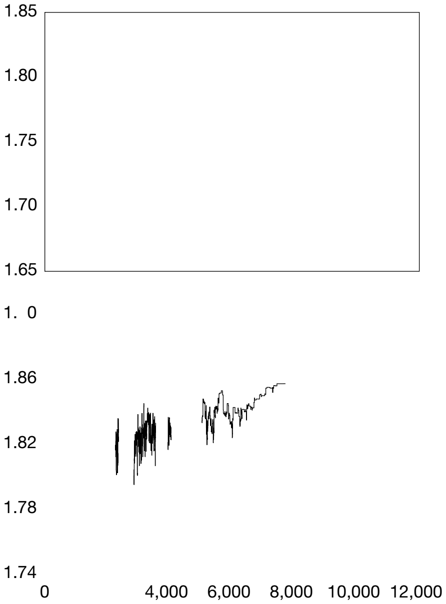
We describe here a solution to the `inverse band-structure problem' based on a direct exploration of the space of atomic con®gurations in search of the con®guration possessing given electronic properties. The formidable complexity of this problem is best illustrated by an example. Consider a pseudo-binary substitutional alloy A B$_{1-}$ C of composition , 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 con®gurations is $N_{\text{config}} = N!/((\ N)!(N - \ N)!)$. For instance, for $= 0.25$ and $2N = 128$, $N_{\text{config}} \approx 10^{14}$. Each con®guration has, in principle, a different electronic structure, and therefore different electronic and optical properties. How many atomic con®gurations (N_{search}) is it necessary to explore in order to ®nd the con®guration that has the target electronic properties? Clearly, if this approach is to be successful N_{search} should be small compared to $N_{\text{con®g}}$. We search the con®guration space using a simulated-annealing algorithm that is able to `learn the system' relatively quickly ($N_{\text{search}} \approx 10^4$) by retaining only those con®gurations 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 con®guration of systems containing a few hundred atoms.

We consider substitutional systems described by an underlying lattice structure of N sites. An atomic con®guration σ is de®ned as a set of N `occupation variables' $\{S_1, S_2, \cdots S_N\}$, where S denotes the identity of the atom located at lattice site . The con®guration variables $\{S\}$ can be restricted to describe a particular experimental growth sequence, for example an A B, A B … superlattice (where , , , denote the number of monolayers) oriented in the [001] direction. We then consider a set of electronic-structure properties $P_\alpha(\sigma)$, de®ned for every con®guration σ, and the corresponding target properties P_α^{target}. The subscript α identi®es speci®c properties, such as bandgaps, effective masses or oscillator strengths. The N-variable object function

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

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

(1) *E[illegible]*. The simulated-annealing technique is an ef®cient algorithm for ®nding the global minimum of a multi-variable, multi-valley function. Given an atomic con®guration σ, a trial con®guration σ_{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 con®guration σ_{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 ®ctitious temperature parameter. By slowly decreasing the temperature to zero, the system is allowed to settle into the con®guration that minimizes the object function O. We use an exponential temperature pro®le $T = T_0\exp(- /\tau)$, where T_0 is the initial temperature and τ is the temperature decay rate. Here [illegible] is the index of the simulated-annealing steps; each simulated-annealing step includes several elementary moves. The exponential temperature pro®le 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 con®guration. We can detect and avoid local minima by changing the initial con®guration and/or the temperature pro®le.

(2) *E* [illegible] *fa* [illegible] *a* [illegible] *a* [illegible]. 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 con®guration (that is, without interchange of atoms). This task is accomplished using a valence-force-®eld method[5] whose parameters are ®tted to *a* [illegible] total-energy calculations for various con®gurations. The outputs are the equilibrium atomic positions $\{\ , \ = 1 \ldots N_{\text{at}}\}$ of the selected con®guration.

Second, realistic hamiltonian: it is well known[6] that the conventional ®rst-principle description of optical properties Ð the local-density approximation (LDA) to density-functional theory Ð 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 con®guration 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 Al

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Acknowledgements

This work was supported by the US Department of Energy, Office of Science, Division of Materials Science.

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