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Short Note

A note on the *virtual crystal* approach to alloy optimization

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In [1], molecular design problems are addressed via a *continuous* formulation. The idea is to allow *fractional* values of what in the natural formulation of the problem are *integer* values. In the alloy optimization context [2], this means we allow fractional occupation of *lattice sites*. For a binary alloy A_cB_{1-c} (the *composition* $c \in [0,1]$ specifies the proportion of A versus B atoms in the system), the identity of the "atom" at each of N lattice sites is represented by a coefficient $x_i \in [-1,1]$ giving the proportion of atom A ($x_i = -1$) versus atom B ($x_i = 1$) at that site. Then, given a fixed alloy supercell, atomic configurations are represented by real vectors x, and properties of a material can be expressed as functions $f(x)$. Now the gradient ∇f with elements $\partial f/\partial x_i(x)$ exists, so we can hope to design materials by solving the continuous, bound-constrained problem $\min_x f(x)$ s.t. $x_i \in [-1,1]$. In integer programming, such a formulation is called a *relaxation* [3]. In mechanics this approach is known as *topology optimization* [4]. In the alloy context we call it the *virtual crystal* (VC) [5] formulation. Here we elucidate several key properties of this approach. In particular:

(1) Because the continuous formulation allows *gradients* to be utilized, it is a vast improvement over a discrete search algorithm where it is applicable.
(2) For the method to succeed without imposing more than bound constraints, *the extrema of the continuous problem must lie close to extrema of the discrete problem.*
(3) Attempts to impose *physicality* as a constraint will not succeed; we always find the closest feasible point to the bound-constrained extremum.
(4) Imposing a *composition* constraint is problematic; in fact, for *any* objective function having the symmetry of an underlying lattice, there is *always* an extremum at exactly the most *unphysical* point.

For our work in electronic structure optimization, we make use of the following: for an electronic state ϵ with wave function ψ that is a solution to the Schrödinger equation $H\psi = \epsilon\psi$, where $H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$, we have the explicit formula

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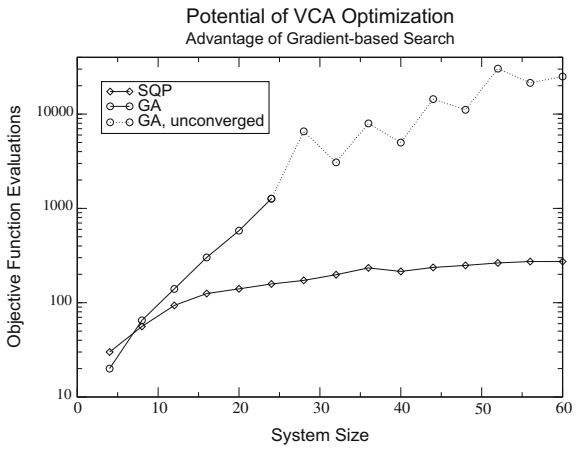

Fig. 1. Scaling of objective function evaluations versus system size (number of atoms) for composition-constrained band gap maximization using a genetic algorithm (GA) and gradient-based constrained optimization method (SQP).

$$\partial\epsilon/\partial x_i = \int \psi^*(r)\frac{\partial V(r)}{\partial x_i}\psi(r)dr. \tag{1}$$

This result is the Hellman–Feyman theorem [6], and it allows us to efficiently calculate ∇f for alloy electronic structure problems.

1. Fig. 1 illustrates why we would want to work with the relaxed problem, even though it introduces possibly unphysical solutions. Shown is a scaling study of a one-dimensional band gap maximization comparing the objective function evaluations necessary with sequential quadratic programming and a genetic algorithm, as a function of the system size. Gradient-based search is *much* faster.
2. In [1], no constraints other than that $x_i \in [-1, 1]$ are imposed, and it would appear that an extremely difficult combinatorial problem has been rendered trivial. Closer examination reveals, however, that success hinges on the fact that fortuitously, *the continuous objective function has an extremum near a physically realizable point*. This requirement on the objective function is the key limitation of the method as stated so far; in order to overcome it, we must impose additional constraints.
3. In order to be *sure* we find structures that are physically realizable, our solution must satisfy the constraint of *physicality* $g(x) = x_i^2 - 1 = 0$ for all *i*. But, in fact, we can *prove* that no matter how we impose the constraint (e.g. gradually imposing it during the search), the method will suffer from the fundamental problem that *the closest feasible point to the bound-constrained minimizer will always be found*. Penalty terms added to *f* to enforce the constraint have the effect of pushing the solution toward the closest feasible point. The dynamics of the optimization are governed completely by the location of

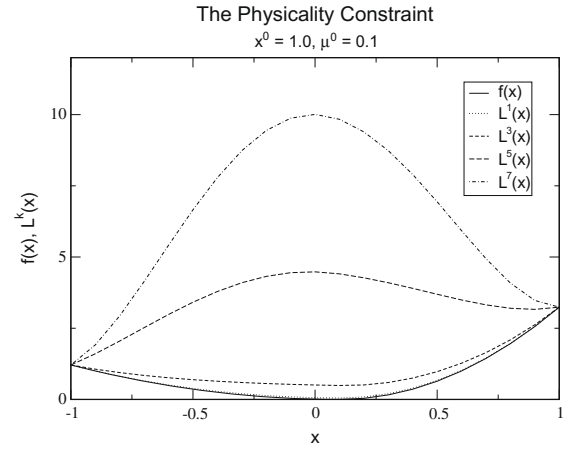

Fig. 2. Illustration of the essential problem with imposing the physicality constraint. The solid line is the objective function $f(x)$. The dotted line close to it is *f* plus a small penalty for violating physicality. Increasing the penalty introduces an increasingly large "hump" in successive functions so that minimizers are gradually pushed *back* to $x^0 = 1$.

the bound-constrained minimum, with no regard to the objective function value at the *feasible* (i.e. physically realizable) points. Fig. 2 illustrates the problem in one dimension. In this case, starting from $x^0 = 1$, the minimizer of the unconstrained problem is $x = 0.1$. After that, increase in the penalty only drives successive minimizers to the right, until we end up where we began.

4. Another important constraint (e.g. for purposes of lattice matching) is the *composition* constraint $g(x) = \sum_{i=1}^{N} x_i - c_{\text{tot}} = 0$, where $c_{\text{tot}} = 2N(c - 0.5)$, by which we force the overall alloy composition to remain fixed. However, consideration of the composition constraint further restricts application of VC optimization: Introducing the constraint via a Lagrange multiplier λ, the first order necessary condition [7] for a constrained optimum is that $\nabla f = \lambda \nabla g$ for some λ. Now, the gradient of the composition constraint is $\nabla g = (1 \cdots 1)^T$. So we are at a constrained extremum if all the partial derivatives of f are the same. This occurs if $x_i = x_j$ for all i, j, because at this point the symmetry of f on the crystal lattice implies that $\frac{\partial f}{\partial x_i} = \frac{\partial f}{\partial x_j}$ for all i, j. Thus for a given composition, there is an extremum at the most *unphysical* part of the VC coefficient domain. Taken together with the case against imposing physicality, this is another serious blow to the VC optimization approach. On the one hand we have seen that we cannot successfully impose physicality, but here we see that in fact for every composition there is an extremum precisely at the most unphysical point, suggesting that without such an imposition we are likely to find *nothing but* unphysical points.

In summary, we have discovered the following about VC optimization: For just the appropriate objective function f, it is a powerful approach. However, one cannot use it for problems requiring the imposition of physicality as a constraint. And consideration of the composition constraint suggests an additional reason *to* impose physicality. How, then, do we profitably incorporate this continuous formulation into the tools of the computational physicist? We have at least two specific ideas, which are under active investigation: First, following the approach of topology optimization, it is possible that an appropriate *nonlinear* interpolation of the underlying atomic potentials will result in an $f(x)$ that has more desirable characteristics; in particular, one for which the bound-constrained extrema are nearly physical. Second, it is possible that the relaxation presented here could enter productively into a heuristic branch and bound procedure in which the continuous formulation provides (possibly unfeasible) lower bounds, while heuristic search supplies (feasible) upper bounds. At present, however, reliable and effective use of the power of gradient information made available by the VC representation awaits the results of these further studies.

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