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Tight-binding total-energy method for transition and noble metals

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A general tight-binding total-energy (TBTE) method is presented that accurately predicts energy differences caused by small perturbations such as those occurring in the evaluation of elastic constants and phonon spectra as well as energy differences from large changes in structure such as structural energy differences, equations of state, and defect energies. Unlike other quantitative TBTE models, no pair potential is required. In addition, we only fit to the band structure and total energies obtained from fcc and bcc first-principles calculations, although we could fit to other data as needed. We have applied the method to 11 transition and noble metals and obtained elastic constants, phonon spectra, and vacancy formation energies in very good agreement with both local-density theory and experiment.

A fast and accurate method of calculating total energies is desirable for the study of large systems including surfaces, extended defects, complex alloys, and amorphous solids; so that molecular-dynamics computations of sufficient length to acquire dynamical correlation functions may be done to study liquids and phase transitions; and so that quantum path integral simulations can be performed accurately. Fast self-consistent techniques[1,2] so far have not lived up to their expectations in that real finite temperature dynamics have not been obtainable due to the enormous computational burden; also, most such methods rely on plane wave bases, and thus are limited to materials for which soft pseudopotentials are available. Potential models have been successful for many materials, but are often limited in accuracy.[3–6] Improvements are achieved by using three- and four-body potentials to account for d-orbital interactions, at the cost of increased complexity.[7–9]

Previous tight-binding total-energy (TBTE) models are similar in many ways to potential models, in that a pair potential is added to a band structure energy,[10–14] both terms determined from a set of parameters fit to first-principles calculations or experiment. TBTE models have been applied successfully to semiconductors and transition metals, but so far they have proven to be less accurate than self-consistent methods. Here we advocate a method that is an extension of and an improvement on first-principles methods. It is at the same level of accuracy as the first-principles methods. Our method is not aimed at unraveling the complexity of first-principles calculations as some other TB models do. Those models do bring in more physical understanding but often require more information, either from experiment or first-principles theory, to make accurate predictions. We first describe the method, and then show applications to transition and noble metals.

One essential feature of TBTE methods that has not been emphasized is the choice of zero for the band structure term. In density-functional theory[15] (DFT) the total energy can be written as

$$E[n(\mathbf{r})]=\sum_{\text{occ}} \varepsilon_i+F[n(\mathbf{r})], \tag{1}$$

where the first term is the "band structure energy." In a self-consistent calculation the eigenvalues ε_i and charge density $n(\mathbf{r})$ are determined self-consistently via the Kohn-Sham[16] equations, whereas in TBTE, the ε_i are determined from a parametrized Hamiltonian, while the remaining functional $F[n(\mathbf{r})]$, which includes the remaining terms from the DFT as well as the nuclear-nuclear repulsion, is parametrized by other means.

Many TBTE models use a parametrized pair potential to represent $F[n(\mathbf{r})]$. However, there is a fundamental problem with this approach that appears not to have been widely recognized. The Kohn-Sham formulation of DFT (Ref. 16) allows the eigenvalues to be shifted by an arbitrary constant V_0, often called the "muffin-tin zero." In self-consistent total-energy calculations the value of this constant is immaterial because the contributions from the constant in each term of Eq. (1) cancel. However, if one separately parametrizes the two terms, the treatment of V_0 becomes all-important.

We have solved this problem by eliminating the pair potential from the tight-binding total energy. This is achieved by choosing the arbitrary zero for each band structure to be such that the total energy is given by the eigenvalue sum

$$E[n(\mathbf{r})]=\sum_{\text{occ}} \varepsilon_i', \tag{2}$$

where $\varepsilon_i'=\varepsilon_i+F[n(\mathbf{r})]/N_e$ is the shifted eigenvalue and N_e is the number of electrons in the system. The challenge is then to find a parametrization which accurately reproduces not only the band structure, represented by the ε_i', but also the total energy. We have found such a procedure and tested it for several transition and noble metals. The method appears to be universally applicable and accurate.

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Previous TBTE models[17–19] determined the tight-binding parameters needed to reproduce the eigenvalue spectrum at a fixed volume. The resulting parameters were then fit as a function of the volume. Instead we construct a set of simple functional forms for the parameters, then adjust the parameters to simultaneously fit the band structure and total energy for a set of volumes and structures. We have used a two-center, nonorthogonal Slater-Koster form.[20,21] The hopping Hamiltonian and overlap parameters are assumed to have the form

$$P_i=(a_i+b_i r)\exp[-c_i^2 r]f(r), \tag{3}$$

where $f(r)=\{\exp[(r-r_0)/\ell]+1\}^{-1}$ is a universal cutoff function chosen to simplify the calculations. At present we take $r_0=16.5$ bohr and $\ell=0.5$ bohr. We restrict ourselves to s, p, and d interactions in the two-center approximation, whence the P_i represent 20 parameters, ten each for the Hamiltonian and overlap matrices. The overlap matrix is a result of the nonorthogonal representation of the orbitals, which we find improves the fit by up to an order of magnitude over the orthogonal representation.

The on-site terms vary as a function of a local "density" around each atom, given by

$$\rho_k=\sum_j \exp[-d_{\tilde{j}\tilde{k}}^2 r]f(r), \tag{4}$$

where $d_{\tilde{j}\tilde{k}}$ depends on atom types $\tilde{k}$ and $\tilde{j}$. ($\tilde{j}$ symbolizes the type of atom j.) The on-site terms D_{lk} for l = s, p, and d for each atom k are then fitted to a finite strain polynomial

$$D_{lk}=e_{l\tilde{k}}+g_{l\tilde{k}}\,\rho_k^{2/3}+h_{l\tilde{k}}\,\rho_k^{4/3}. \tag{5}$$

The parameters $a_{ikk'}$, $b_{ikk'}$, $c_{ikk'}$, $d_{\tilde{j}\tilde{k}}$, $e_{l\tilde{k}}$, $g_{l\tilde{k}}$, and $h_{l\tilde{k}}$ above are simultaneously fit to the band structures and total energies at different structures and volumes. For the metals reported here we fit to $4-6$ volumes in each of the fcc and bcc structures. We have used eigenvalues derived from uniform k-point meshes consisting of 85 and 55 k points for the fcc and bcc structures, respectively. For a monatomic material there are 70 parameters, which must fit approximately 4000 weighted input data. Typically the squared residuals of the occupied or partially occupied bands are weighted ten times more than the completely unoccupied high bands, while the total energies are weighted 200 times more than a single band. Although the parametrization (3) does not require the overlap matrix to be positive definite, we include a penalty function in the fitting procedure which forces the overlap matrix to have this property. Our fitting program used the Minpack package. For the metals reported here, we have achieved average rms errors in the fit of 5 mRy for the occupied bands and 0.5 mRy for the total energies.

The fit is highly nonlinear with many multiple minima, and great care is needed to test the resulting model for reasonable behavior outside the range of the fit. We find that fitting a number of unoccupied bands helps constrain the parameters to have physically reasonable behavior. Similar problems appear when fitting atomistic potentials, so we do not feel that the necessary care will reduce the applicability of the method.

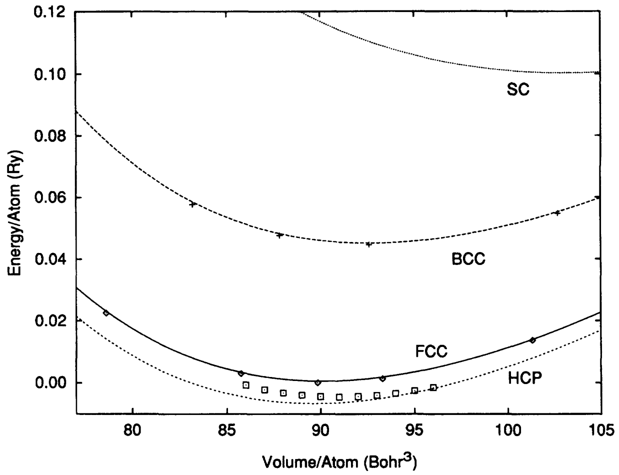

FIG. 1. The equation of state for Ru in several structures, using the TB method outlined in the text. The points indicate total energies obtained from APW calculations. The lines indicate TB energies in the indicated phases. The c/a ratio in the TB hcp phase has been relaxed to a value of 1.58 to minimize the total energy.

We have applied this method to the study of several metals. For Ti, Nb, Mo, Ru, Rh, Pd, Ta, and Ir, we fitted the parameters (3–5) to the band structures and total energies of the fcc and bcc lattices computed by the muffin-tin augmented-plane-wave (APW) method.[17] For Cu, Ag, and Au we used the full-potential linearized-augmented-plane-wave (LAPW) results.[22,23] In all cases we used the Hedin-Lundqvist parametrization[24] of the local-density-approximation (LDA) to the DFT. As a check of the method, we used the parametrization to calculate the energy/volume relationship for the fcc, bcc, hcp, simple cubic, and diamond phases for each metal.

In all of these cases, *including the hexagonal metals Ti and Ru*, the TB method correctly predicted the ground state structure, even though we used only first-principles data from the fcc and bcc phases. We show the results for Ru in Fig. 1. Note that the TB method gives the hcp structure (which was not fitted) lower than the fcc, in agreement with experiment, but it increases the hcp-fcc energy difference by 2 mRy over the APW values, as shown in Fig. 1. The simple-cubic and diamond structures are well above the bcc structure in energy, as expected. In the case of Ti we obtain again the hcp structure in the correct order, but the hcp-fcc distance is increased by 4 mRy. This is possibly a result of fitting to a muffin-tin first-principles calculation. We are currently refitting the parameters to the full-potential energies and eigenvalues to determine if this will improve the hcp-fcc energy difference.

We next applied the TB method to the calculation of elastic constants. The LDA successfully reproduces experimental elastic constants, if the calculations are performed at the experimental volume.[25–27] Using tight-binding parameters obtained from fits to the fcc and bcc structures, we calculated the elastic constants within the TB using the same techniques as in previous first-principles calculations.[26] No strained structures were included in the input data set, so the elastic constants are predictions of the model rather than tests of the fit. In Fig. 2 we show the shear elastic constants for the

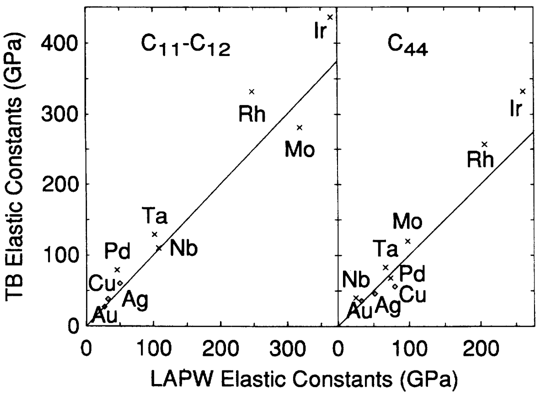

FIG. 2. Shear elastic constants computed with the TB formulation of this paper, compared to first-principles LAPW calculations. On the left we show $C_{11}-C_{12}$, and on the right C_{44}. Points denoted by ◇ are from TB parameters fitted to full-potential LAPW band structures and energies, while points marked × are from TB parameters fitted to muffin-tin APW results.

nonmagnetic cubic materials in our sample, compared to our first-principles full potential LAPW results.[25–27] The best TB elastic constants are for Cu, Ag, and Au, where all elastic constants are within 10 GPa of the LDA values, and where we fitted the TB parameters to match the full-potential energies and band structures in the fcc and bcc phases. Several of the APW fitted materials (Nb, Mo, and Ir) are of comparable accuracy. On further analysis, we find that in these cases the muffin-tin APW prediction of the fcc-bcc energy difference is almost identical to the full-potential LAPW energy difference. From this we conclude that fitting to full-potential first-principles calculations will produce elastic constants in agreement with the LDA values.

Our next calculations used the tight-binding method to determine the phonon spectrum. We anticipate that this will be one of the major applications of this method in the future, since first-principles calculations[28] are rather slow, while atomistic potential models have difficulty in reproducing the phonon spectra of bcc metals,[29] unless many-body interactions are included.[7] We used supercells of up to 16 atoms to calculate phonon frequencies in the frozen-phonon approximation.[30] Figure 3 compares our results with experiment,[31–34] and to a limited set of first-principles results. Our phonon frequencies are mostly larger than the experimental values, especially near the edge of the Brillouin zone. Our most encouraging result is the prediction for the behavior of Nb near the zone edge. In particular, we reproduce the experimentally observed[33] crossing of the longitudinal and transverse modes near H. This behavior is not observed in standard embedded atom models (EAM),[29] and only a careful choice of parameters reproduces this result in empirical tight-binding calculations.[35] We note that our calculations may have some difficulties in other parts of the Brillouin zone not shown here. We are continuing this work to determine if a better fit to the first-principles fcc and bcc results will improve our calculations. If extremely accurate phonon frequencies are desired, of course, we can fit our TB parameters to self-consistent frozen phonon calculations at high symmetry points in the Brillouin zone, where the supercell method allows us to use a small number of atoms. In this way we should be able to obtain higher accuracy, comparable to that of the EAM in fcc metals.[36]

As a final demonstration of the power of this method, we use it to calculate the vacancy formation of silver within the supercell approximation.[37] First-principles calculations[37–41] using this method are difficult because of the "order N^3" problem. Large unit cells, required to limit the interaction between vacancies, are not generally possible, especially for d metals. We used the TB method to calculate the vacancy formation energy for silver, both with and without relaxation around the vacancy, using unit cells containing up to 216 sites, although for this problem the formation energy was essentially converged for unit cells with 128 atoms. Without relaxation, we found a vacancy formation energy of 1.31 eV. Including relaxation, our predicted formation energy was 1.24 eV, somewhat larger than the experimentally observed value of 1.05 eV.[42]

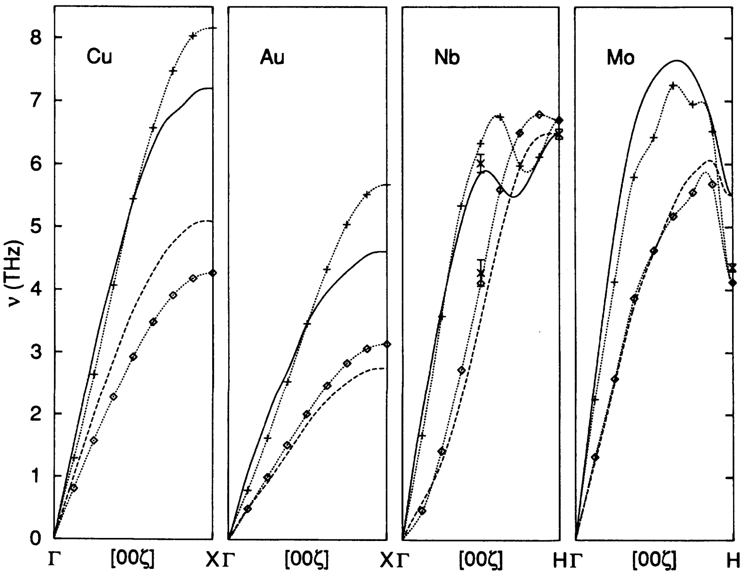

FIG. 3. Phonon frequencies computed by the TB method in the [100] direction for Cu, Au, Nb, and Mo. The (solid, dashed) lines are spline fits to the experimental data for the (longitudinal, transverse) mode. The (+, ◇) indicate the TB (longitudinal, transverse) frequencies. The dotted lines are spline fits between these points. The × represent full-potential LAPW calculations at selected points and polarizations, with our estimate of the uncertainty.

In conclusion, we have developed a total-energy tight-binding method which allows an accurate interpolation from the fcc and bcc structures to the hcp and simple cubic structures, as well as the distorted phases necessary to obtain elastic constants, phonon spectra, and vacancy formation energies. The method correctly predicts the ground state structure of many metals, including the prediction of an hcp ground state for Ti and Ru, without using the hcp phase as input. The method has also been applied to the calculation of elastic constants, phonon frequencies, and vacancy formation energies. We have obtained good agreement with both first-principles results and experiment for structures far removed from the fcc and bcc lattices used to determine the parameters. Some of the discrepancies can apparently be removed by fitting the parameters to full-potential results rather than muffin-tin calculations. If this is not sufficient, the method can be easily extended including other crystal structures in the parameter fit. It should be emphasized that the proposed method is orders of magnitude faster than the state-of-the-art LDA-based electronic structure methods, and when extended beyond monatomic it will efficiently and accurately calculate phonon spectra and defect energies for metals. The method is comparable in accuracy to the best atomistic potential model.[7]

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