

TIGHT-BINDING HAMILTONIANS

D.A. Papaconstantopoulos

Condensed Matter Physics Branch

Naval Research Laboratory, Washington, DC 20375-5000

1. INTRODUCTION

The use of tight-binding (TB) Hamiltonians as a starting point of many theories is common place in condensed matter physics and materials science. The construction of such Hamiltonians is done with two different philosophies in mind. One is based on atomic level values and the idea of choosing a very small number of hopping integrals usually involving only d orbitals.¹⁻³ The other approach is in the spirit of the Slater-Koster (SK) interpolation^{4,5} method which consists of a fit to the results of a band structure calculation and can easily incorporate hybridization of the d with the s-p orbitals. The practitioners of the first approach wish to retain simplicity in their model and physical significance of the values of their TB parameters. They achieve this at the expense of using a TB Hamiltonian that produces energy bands and densities of states which are of limited accuracy. On the other hand the second approach with the possible deficiency that occasionally produces opposite signs of certain small parameters, can be made to agree, especially for transition metals, almost exactly to the band structure derived from the first principles methods.⁵

2. REPRESENTATIVE RESULTS

In Fig. 1 we demonstrate⁶ for Nb the very substantial differences found between the energy bands based on the Harrison solid state table and a 6x6 Hamiltonian (s+d orbitals) and those obtained from a SK type fit that corresponds to a 9x9 Hamiltonian (s+p+d orbitals). One can see that along the directions ΓH , ΓN , and ΓP the energy bands have entirely different shapes. In particular the position of the Fermi level, E_F , to be above the state $\Gamma_{25'}$ for the Harrison Hamiltonian (HH) and below $\Gamma_{25'}$ in our calculation is a striking difference that produces the wrong Fermi surface in the HH calculation. In addition, the non-inclusion of p-states in HH places the higher energy bands at too high energies which would prevent any serious comparison with experiments probing the excited states.

Reference 5 contains tabulations of SK parameters of 53 elements in the periodic table. These parameters were derived by fitting to first principles band structure calculations. Four different sets of SK parameters are given involving two and three center integrals as well as orthogonal and non-orthogonal basis. In most cases the energy bands are fitted very well with an rms deviation of the order of 1 mRy. The Fermi level values of the densities of states (DOS), its angular momentum decomposition, the Fermi velocity and plasmon energy together with energy band and DOS figures are presented for each element.

These TB Hamiltonians (TBH) can be used in a variety of applications concerning disordered materials, surfaces, interfaces, defects, phonon spectra, etc. We have applied the TB coherent potential approximation

(CPA) formalism in many disordered systems. Our general conclusion⁷ is that for substitutional alloys between neighboring elements in the periodic table the TB-CPA results are in excellent agreement with those of the KKR-CPA theory.⁸ This is demonstrated in Fig. 2 where a comparison of the DOS between TB-CPA and KKR-CPA is given for the disordered alloy $\text{Pd}_{0.5}\text{Ag}_{0.5}$. Indeed the two calculations agree exceptionally well in all the details of the density-of-states spectra. We have found that the TB-CPA (within the diagonal disorder formulation) doesn't work as well when elements from different rows of the periodic table are involved. For example in the Cu-Pd system we have found substantial differences from the KKR-CPA results. It appears that in such alloys significant charge transfer occurs and therefore charge self-consistency and off-diagonal disorder are important. Indeed we have included in the formalism⁹ the effects of off-diagonal disorder and results showed a substantial improvement.

Another interesting application of the TB-CPA is in hydrogenated amorphous Si.¹⁰ In this case the TB-CPA is particularly convenient because of the ease that one can incorporate a variety of atomic configurations that involve the replacement of Si atoms by either vacancies or vacancies whose dangling bonds may be decorated by 1-4 hydrogen atoms. This kind of approach despite its underlying crystallinity gives remarkable agreement to the experimental results of the amorphous state including XPS and absorption coefficient data.

We have also applied TBH to the study of interfaces.¹¹ Specifically, we have studied the Fe-Ge (110) interface which required 7 layers of Fe with 4 atoms each and 11 layers of Ge with 2 atoms each for a total of 50 atoms in the unit cell. Such a calculation is beyond the capabilities of present supercomputers if it were to be carried out in a self-consistent first principles way. Our results clearly identify the interface states and are consistent with the reactive nature of this interface seen in experimental studies.

Another use of TBH is that described in this volume by de Fontaine¹² where the generalized perturbation method and the cluster variation method are used together with the CPA. This approach brings together quantum and statistical mechanics to evaluate phase diagrams for a variety of alloys.

Finally TBH become a very valuable basis for the study of the new high temperature superconductors. We have already¹³ constructed a TBH for the La_2CuO_4 compound. In this work we have fit first principles LAPW band structure results by the SK method using an orthogonal 31-orbital basis that includes La-d, Cu-s,p,d and O-p orbitals. This fit requires 44 two-center parameters obtained by fitting to the LAPW results at 71 k-points in the irreducible tetragonal Brillouin zone. The rms deviation from the LAPW eigenvalues is 14 mRy for the lower 17 bands. In order to obtain an accurate DOS near the Fermi level, E_F , we used an increased weight around E_F . The resulting DOS is shown in Fig. 3 where it is important to note that E_F falls just above a van Hove singularity that has been associated with the enhancement of the superconducting transition temperature upon doping with Ba or Sr. Calculations that account for oxygen vacancies and rare earth substitutions using the CPA are now in progress.

Other applications of the use of accurate TBH are in the evaluation of the electron-phonon interaction and the first principles determination of phonon dispersion curves.¹⁴ Also, recently Fry et al.¹⁵ have employed the two-center orthogonal SK parameters of Ref. 5 to compute the many-body-enhanced magnetic susceptibility for paramagnetic bcc Mn.

Acknowledgement

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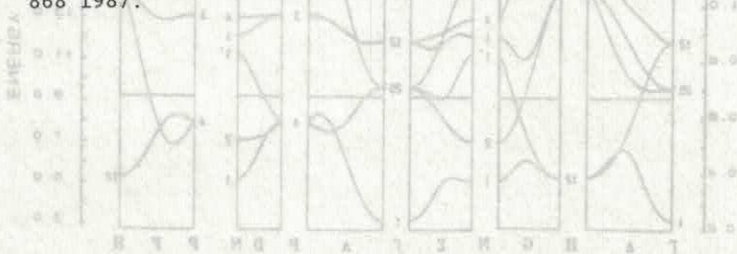


FIGURE 1. The top panel shows the energy bands of 3k calculated using Harrison's 3k parameters and the bottom panel shows the energy bands of 3k calculated using the 3k parameters of Ref. 2.

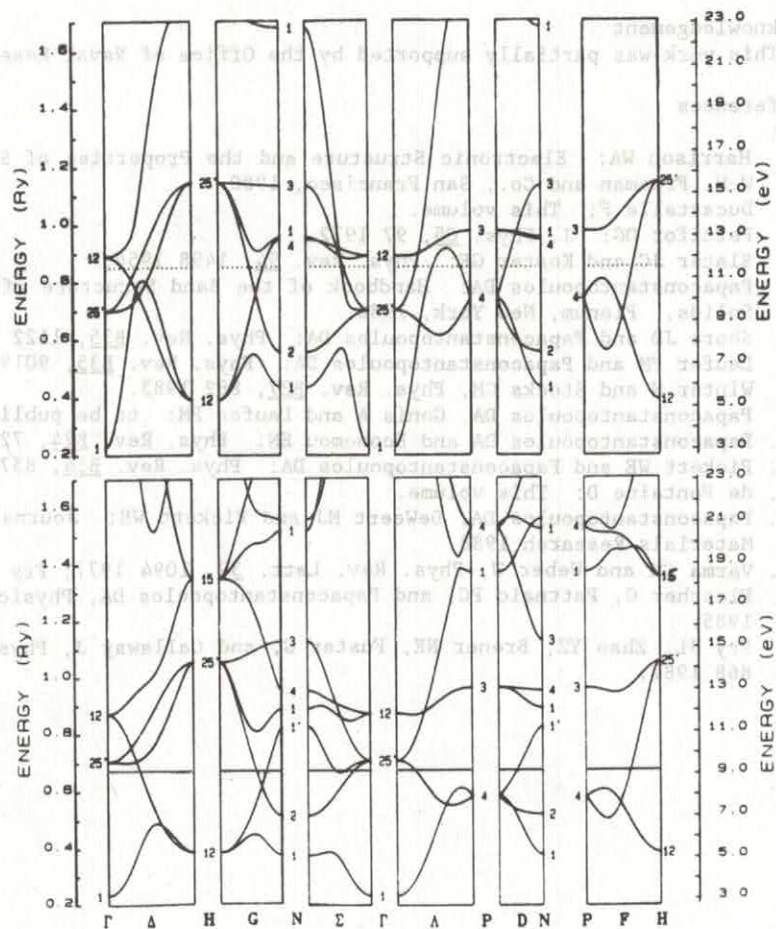


FIGURE 1. The top panel shows the energy bands of Nb calculated using Harrison's SK parameters and 6x6 Hamiltonian. The bottom panel shows the energy bands of Nb calculated using the Sk parameters of Ref. 5.

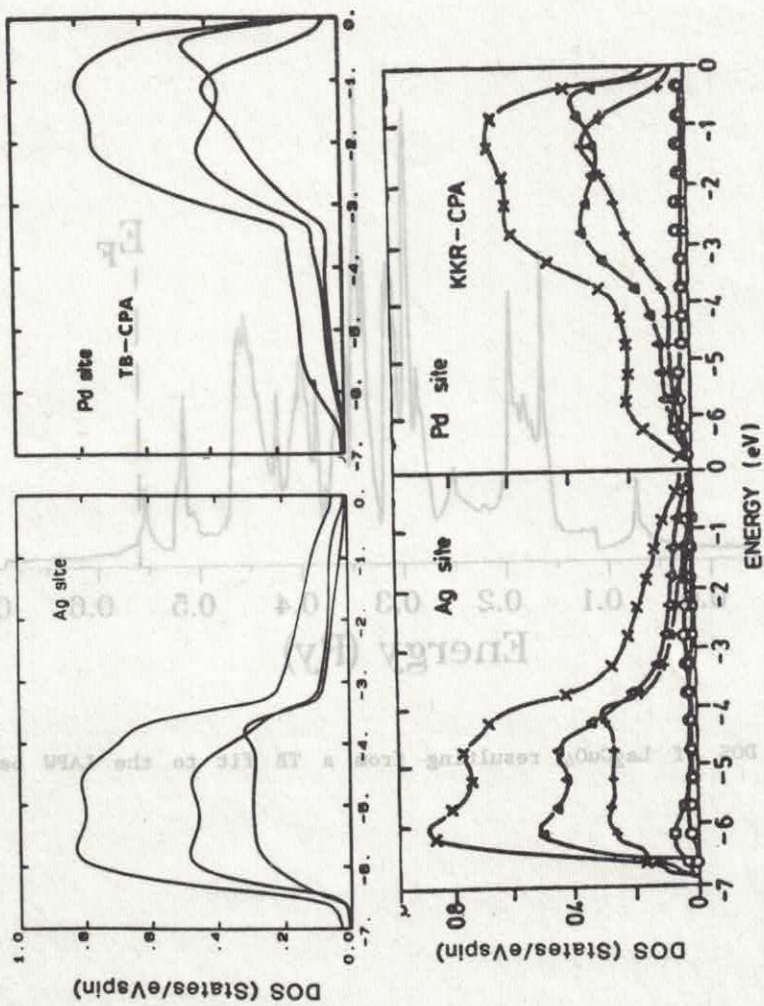


FIGURE 2. Comparison of TB-CPA and KKR-CPA densities of states for $\text{Pd}_{0.5}\text{Ag}_{0.5}$. Each panel shows the total, t_2g and e_g DOS per site.

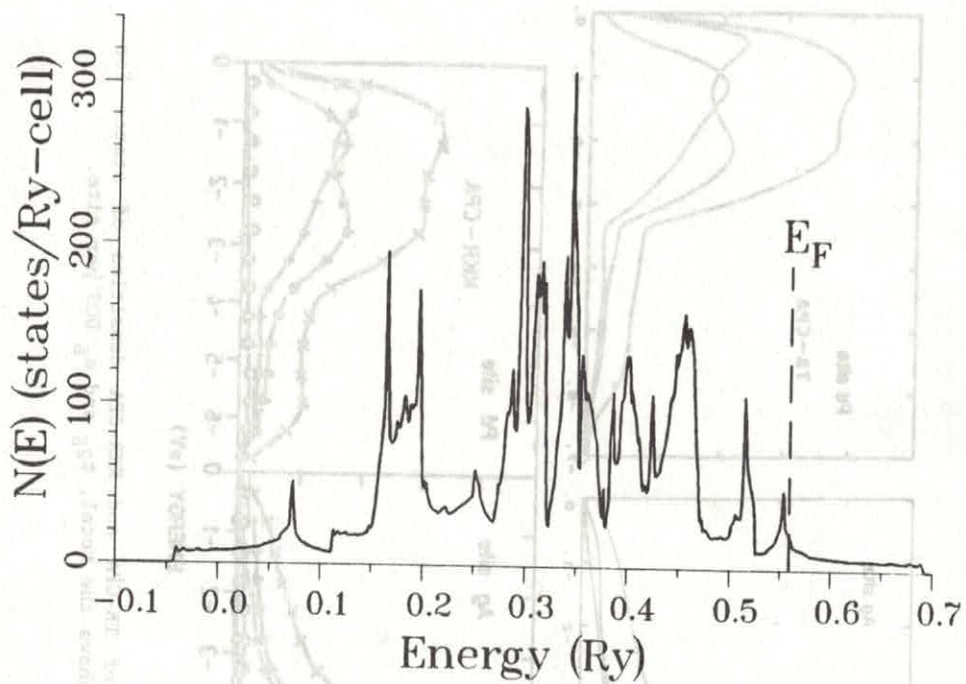


FIGURE 3. DOS of La_2CuO_4 resulting from a TB fit to the LAPW band structure.