Modifications and extensions to Harrison's tight-binding theory

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Harrison's tight-binding theory provides an excellent qualitative description of the electronic structure of the elements across the periodic table. However, the resulting band structures are in significant disagreement with those found by standard methods, particularly for the transition metals. For these systems we developed a procedure to generate both the prefactors of Harrison's hopping parameters and the onsite energies. Our approach gives an impressive improvement and puts Harrison's theory on a quantitative basis. Our method retains the most attractive aspect of the theory, in using a revised set of universal prefactors for the hopping integrals. In addition, a new form of onsite parameters allows us to describe the lattice constant dependence of the bands and the total energy, predicting the correct ground state for all transition, alkaline earth, and noble metals. This work represents not only a useful computational tool but also an important pedagogical enhancement for Harrison's books.

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I. INTRODUCTION

Harrison developed an elegant analytic theory of the electronic structure of solids.[1,2] This theory has been very successful in providing a physical understanding of the electronic structure and the characteristics of bonding. However, Harrison's theory of solid state has limited ability to produce accurate numerical results for the band structure, density of states, and the relative stability of different crystal structures.

In this work, we describe Harrison's approach on quantitative foundation. We have now realized that it is possible to put the Slater–Koster parameters in the form given by Harrison but with new prefactors and determine new onsite parameters. The result is that we retain the universality of Harrison's parameters, which means the same prefactors for all transition, alkaline earth, and noble metals, but with different onsite terms for each element. It is clear to us that this approach, perhaps slightly modified, may be extended to cover the rest of the periodic table. We have also succeeded with a small number of additional parameters to describe the volume and structure dependence of the energy bands and, therefore, obtain total energies and predictions of relative stability.

Harrison has opted for simplicity in the LCAO approach and has created a set of universal hopping parameters that can easily be used to perform calculations. In the tables of his books, Harrison uses atomic energies as onsite parameters in his Hamiltonians, which is the main shortcoming of directly using these tables, to perform sufficiently accurate band structure calculations. However, Harrison pointed out[2] that atomic values for the *d*-state energies need to be corrected for differences in *d*-state occupancy, and gave a way for doing that in the case of Cr.

We illustrate the importance of correcting the values of the onsite parameters for the transition metals Nb and Pd by using Harrison's hopping parameters and uncorrected atomic term values. We compared the results of a 6×6 Harrison Hamiltonian (without *p* orbitals) as given in Harrison's book and we found that the energy bands created this way are in serious disagreement with augmented plane wave (APW) re-

sults (left hand side, Fig. 1). We also tested a 9×9 (with *p* orbitals) Harrison Hamiltonian with all hopping prefactors kept at Harrison's values, but the onsite parameters modified by fitting the energy bands to APW calculations.[3,4] This
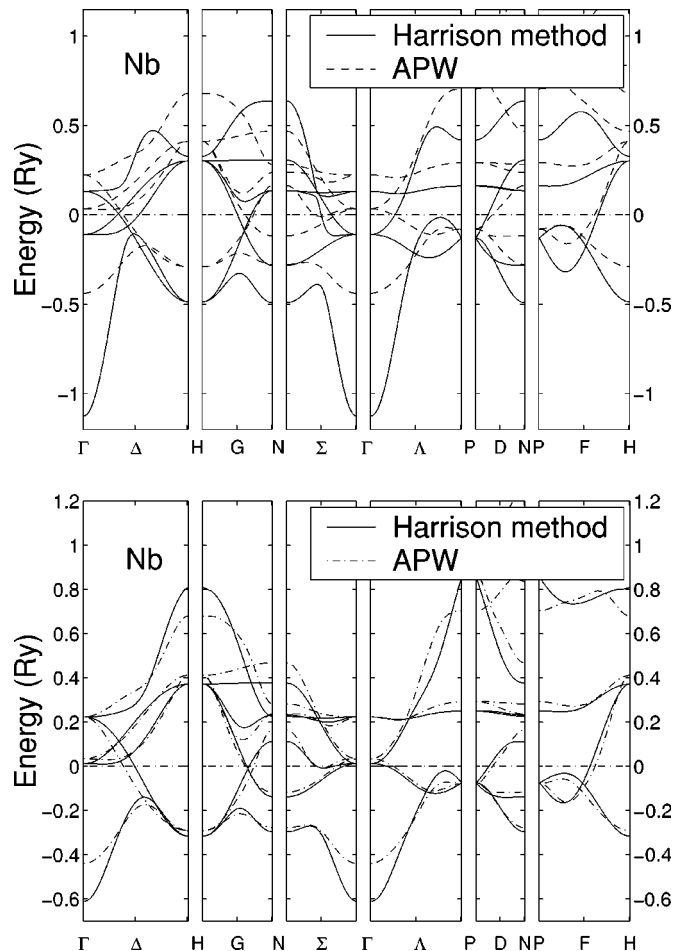

FIG. 1. Harrison's energy bands of Nb compared to APW. Left graph created by 6×6 Hamiltonian; right graph created by 9×9 Hamiltonian and fitted onsite energies.
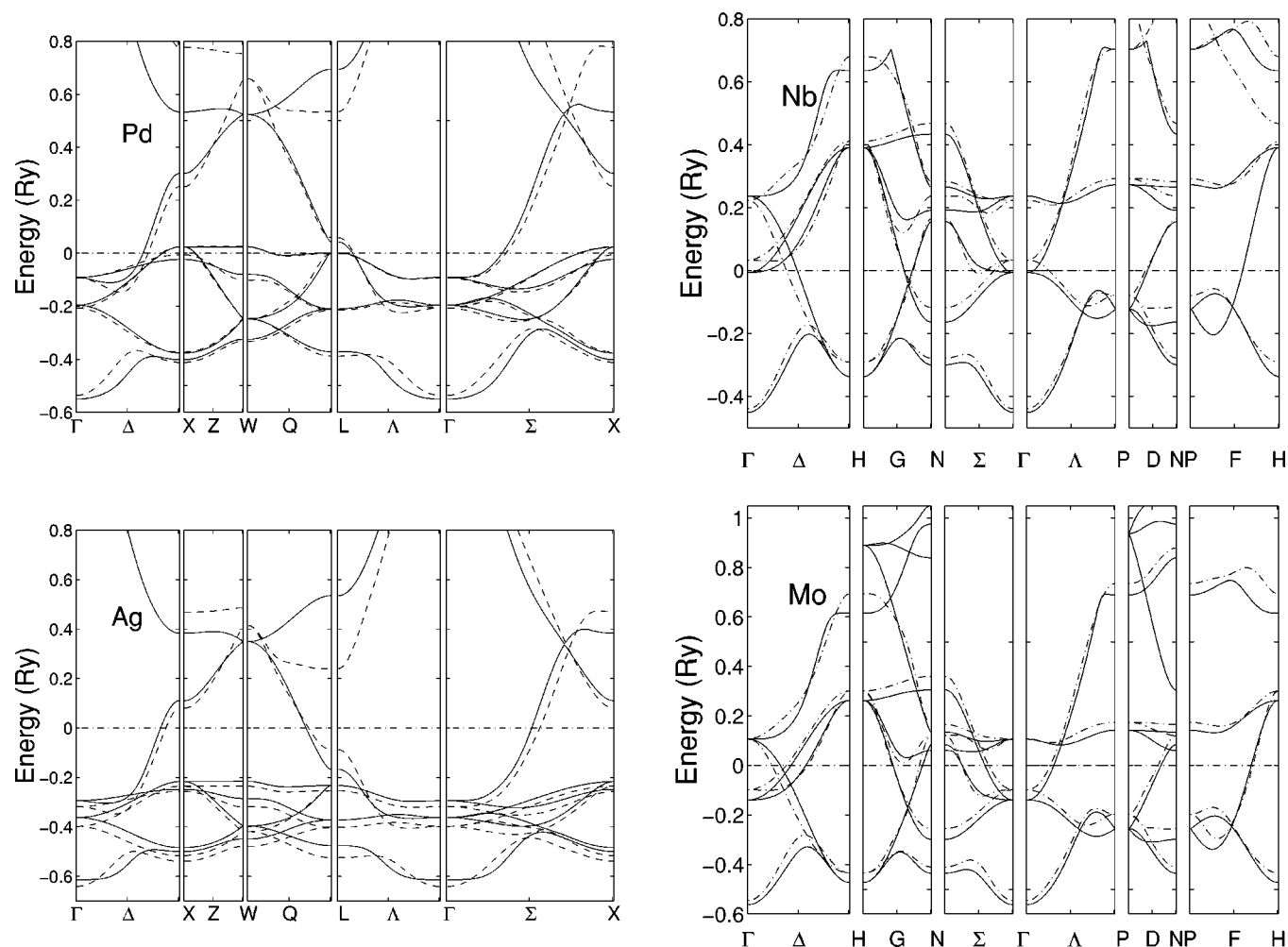
FIG. 2. APW and modified Harrison's energy bands of Ag, Pd, Nb, and Mo. The solid line is the modified Harrison result and dash–dotted line is the APW result.

modification gave us better results in the d bands, but there was still a large error for the s-like first band (right-hand side Fig. 1). Our conclusion is that Harrison's theory can only give a qualitative description of the band structure of the transition metals even if we fit the onsite terms to first-principles results.

II. ENERGY BANDS AND DENSITY OF STATES

We have developed a procedure that while maintaining the simplicity of Harrison's approach gives an impressive improvement that puts the theory on a quantitative basis. To accomplish this we have made the following modifications to Harrison's theory: (1) We introduced a p onsite energy as an additional parameter to the s and d onsite energies used by Harrison, and fit them all to APW results. (2) We modified the sp hopping integrals of Harrison, by introducing a dimensionless parameter γ_s as follows:

$$V_{ll'm} = \eta_{ll'm} \frac{\gamma_s \hbar^2}{m_e d^2}. \tag{1}$$

The parameter γ_s provides more flexibility to fit the first and sixth bands. (3) We obtained new hopping prefactors by si-

multaneously fitting the APW energy bands of the following 12 transition metals: V, Cr, Ni, Cu, Nb, Mo, Pd, Ag, Ta, W, Pt, and Au. In this fit, all 12 elements have the same common prefactors $\eta_{ll'm}$ but different (for each element) onsite energies s, p, and d, and also different values for the parameters γ_s and r_d that appear in the hopping parameters. Our Hamiltonian corresponds to an orthognal basis set as in Harrison. We did the above fitting at the equilibrium lattice constants of the structure, which is the ground state of each element, and included interactions of nearest, second-nearest, and third-nearest neighbors for the bcc structure and nearest- and second-nearest for the fcc structure. Of course, using more neighbors than Harrison did in the fit would automatically make changes in the parameters, even if one were fitting the same bands. Using the parameters determined with the above procedure, we reproduced APW energy bands and density of states (DOS) remarkably well, not only for the 12 elements originally fitted, but also for the rest of the transition metals, the alkaline earth and the noble metals, as seen in Figs. 2 and 3 for four of the elements. Our new Hamiltonian prefactors, common for all metals, together with Harrison's original prefactors are shown in Table I. The onsite terms and the parameters γ_s and r_d for each element are shown in Table II.
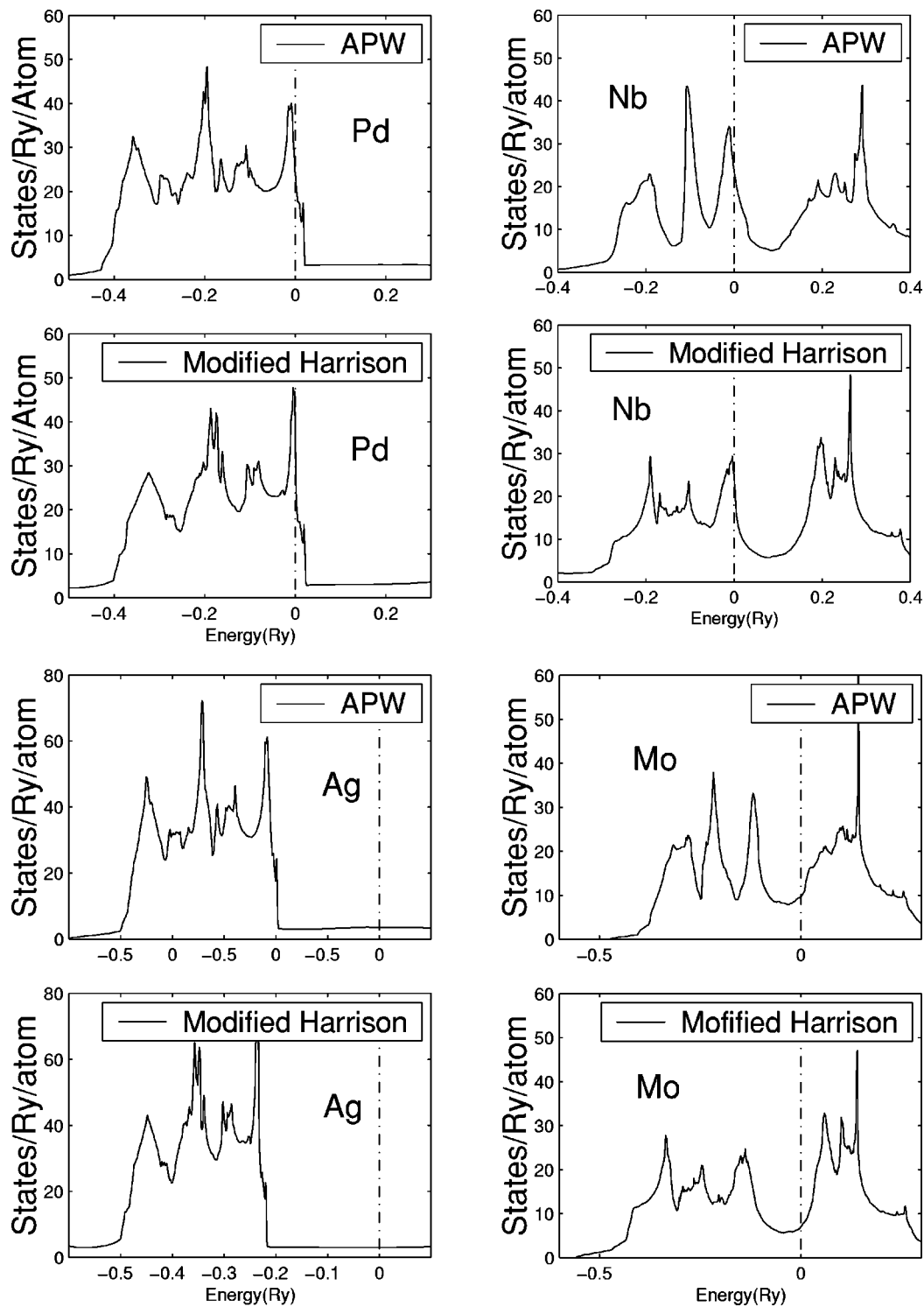
FIG. 3. APW and modified Harrison's density of states of Ag, Pd, Nb, and Mo.

We used the prefactors of Table I with new onsite energies γ_s and r_d to fit the rest of the transition metals, including those with hcp ground states. For the hcp metals, we fitted energy bands of fcc structures at the equilibrium lattice, and found that our parameters produce good transferability, i.e., reproduced the hcp energy bands very well without fitting them. The hcp energy bands of Ti and Ru are shown in Fig. 4. We also fitted energy bands of the ferromagnetic elements Fe, Co, and Ni, and calculated magnetic moments of the three elements at the experimental lattice constant. Table III shows good agreement of magnetic moments of Fe, Co, and Ni with experimental values.

III. TOTAL ENERGY

Next we address the issue of fitting total energy results. In order to do this we follow the Naval Research Laboratory

TABLE I. Harrison's hopping prefactors and our modified values.

	$\eta_{ss\sigma}$	$\eta_{sp\sigma}$	$\eta_{pp\sigma}$	$\eta_{pp\pi}$	$\eta_{sd\sigma}$
Harrison	−1.32	1.42	2.22	−0.63	−3.16
Modified Harrison	−0.90	1.44	2.19	−0.03	−3.12
	$\eta_{pd\sigma}$	$\eta_{pd\pi}$	$\eta_{dd\sigma}$	$\eta_{dd\pi}$	$\eta_{dd\delta}$
Harrison	−2.95	1.36	−16.2	8.75	−2.39
Modified Harrison	−4.26	2.08	−21.22	12.60	−2.29

TABLE II. Onsite parameters, γ_s and r_d.

| Name	s(Ry)	p(Ry)	d(Ry)	γ_s	r_d(a.u.)
K	0.26067	0.22200	0.25426	1.13081	3.65981
Ca	0.11994	0.24522	0.03657	1.07535	2.66618
Sc	0.14809	0.38903	−0.06695	0.98860	2.12358
Ti	0.51352	0.79759	0.21879	0.92307	1.85267
V	0.64331	0.73136	0.04711	0.90164	1.65358
Cr	0.76372	0.86088	0.06389	0.87733	1.51087
Mn	0.47377	0.86874	−0.00300	0.82491	1.42366
Cu	0.54432	0.93013	−0.05425	0.92178	1.23548
Zn	0.44779	0.77968	−0.10598	0.78430	0.97054
Sr	0.32339	0.41296	0.22810	1.22463	3.29024
Y	0.29652	0.51778	−0.07450	1.19367	2.75073
Zr	0.54322	0.87432	0.17820	1.15726	2.40732
Nb	0.85097	0.99247	0.24572	1.08802	2.19244
Mo	0.83057	0.97345	0.10805	1.06314	2.01708
Tc	0.64629	1.08072	0.09302	1.00014	1.91300
Ru	0.65130	1.07465	0.04760	1.00001	1.80799
Rh	0.68579	1.06923	0.06445	0.99989	1.71702
Pd	0.57192	0.95218	0.04268	0.90172	1.63401
Ag	0.44541	0.79565	−0.04959	0.84306	1.52479
Ba	−0.04951	0.03502	−0.20497	1.07269	3.56198
Hf	0.29999	0.75423	0.32239	0.88204	2.50856
Ta	0.70455	0.92990	0.23577	1.12532	2.31790
W	0.64038	0.86882	0.09170	1.11008	2.17888
Re	0.60996	1.15988	0.15348	1.14822	2.08878
Os	0.53044	1.06428	0.05117	1.11453	2.01287
Ir	0.47125	1.01759	0.01404	1.06585	1.91597
Pt	0.43374	0.94903	0.00569	1.00933	1.83802
Au	0.37521	0.84519	−0.02211	0.94002	1.75060
Hg	0.36137	0.68747	−0.10952	0.90569	1.53337
Fe[a]	0.87761	0.84369	0.02940	0.94826	1.33156
Fe[b]	0.84395	0.88024	0.19670	0.93012	1.43124
Ni[a]	0.45155	0.69040	−0.04560	0.72937	1.22004
Ni[b]	0.46394	0.70316	−0.00173	0.73568	1.24548
Co[a]	0.69846	0.68425	−0.06187	0.79695	1.26137
Co[b]	0.66026	0.70002	0.06184	0.77917	1.33184

[a]Ferromagnetic spin up.
[b]Ferromagnetic spin down.
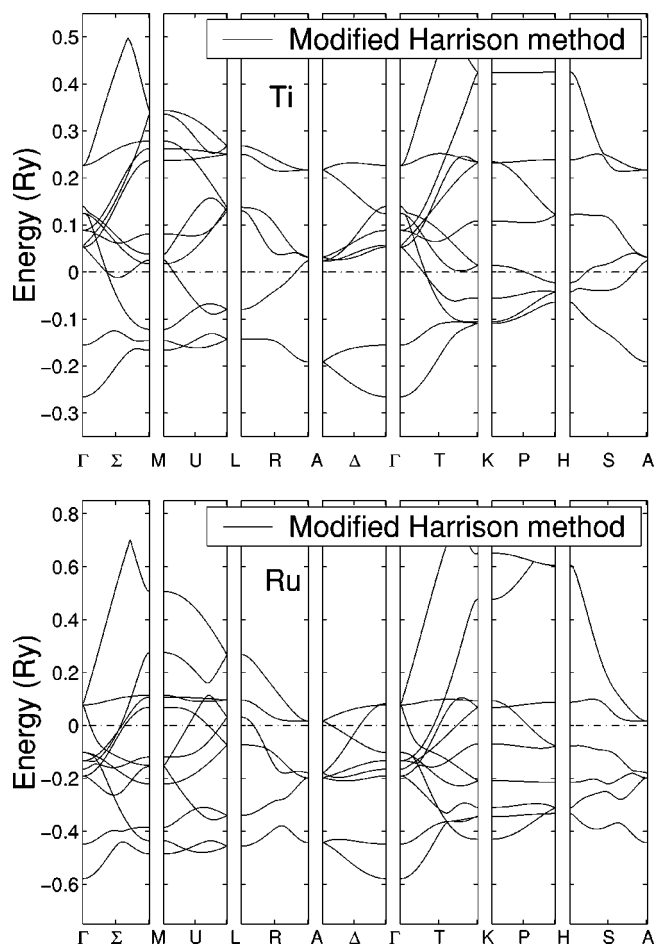
FIG. 4. Energy bands of hcp Ti and Ru.

tight-binding (NRL-TB) methodology,[5,6] which uses parameters which are transferable between structures.[5] In most TB approaches as well as in all the so-called "glue" potential atomistic methods one writes the total energy as a sum of a band energy term (sum of eigenvalues) and a repulsive potential $G[n(r)]$ that can be viewed as replacing all the charge density $n(r)$ dependent terms appearing in the total energy expression of the density functional theory. The NRL-TB method has the unique feature that eliminates G by the following ansatz. We define a quantity V_0:

$$V_0 = \frac{G[n(r)]}{N_e}, \qquad (2)$$

where N_e is the number of valence electrons.

We then shift all first-principles eigenvalues $\epsilon_i(k)$ by the constant V_0 and define a shifted eigenvalue:

TABLE III. Magnetic moments of Fe, Co, and Ni.

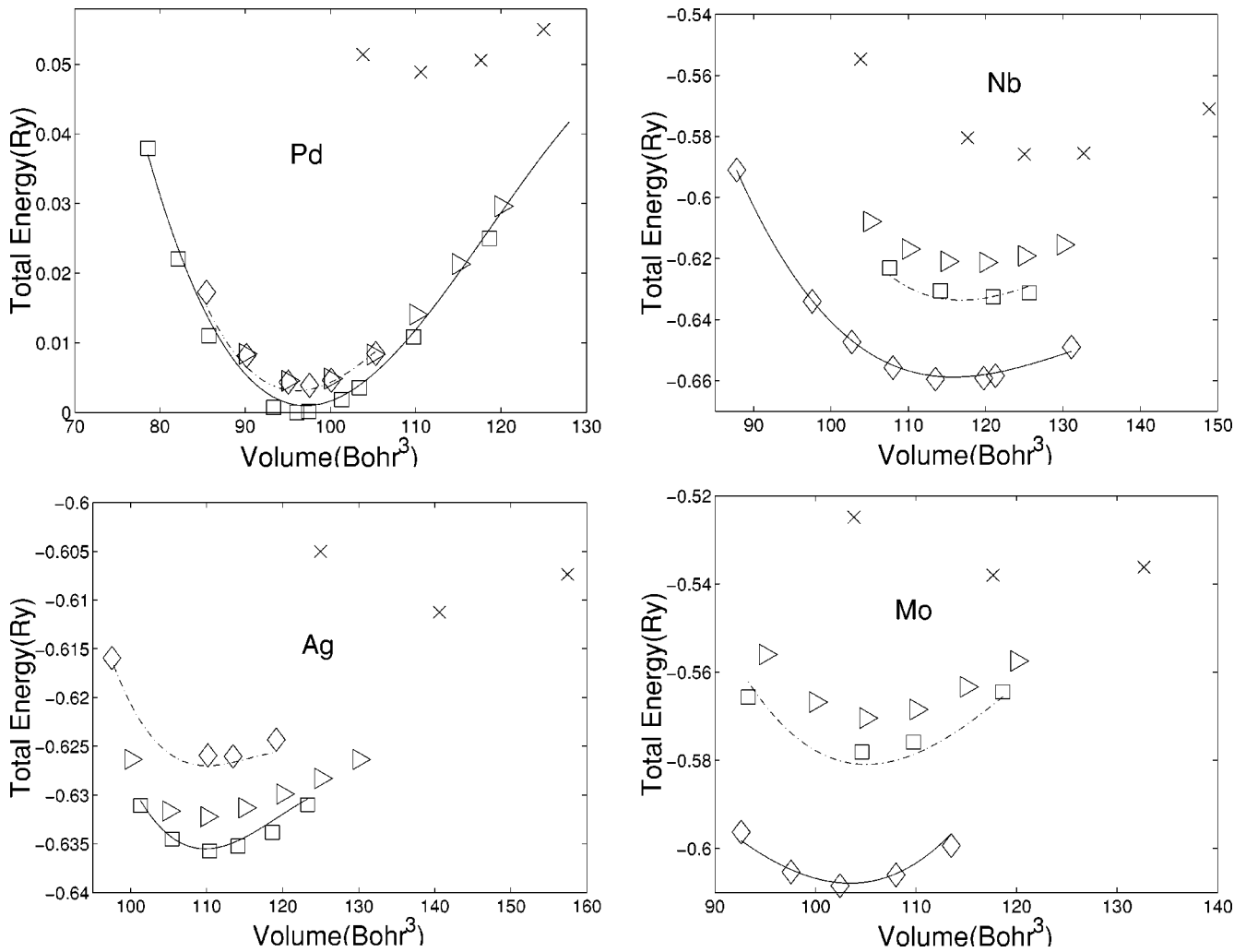| Element	Structure	TB(μ_B)	Exp.(μ_B)
Fe	bcc	2.21	2.22
Co	hcp	1.52	1.72
Ni	fcc	0.56	0.61

FIG. 5. Total energies of Ag, Pd, Nb, and Mo. The solid line denotes bcc APW results and dash–dotted line denotes fcc APW results. The diamond, square, triangle, and X symbols represent bcc, fcc, hcp, and sc TB results, respectively.
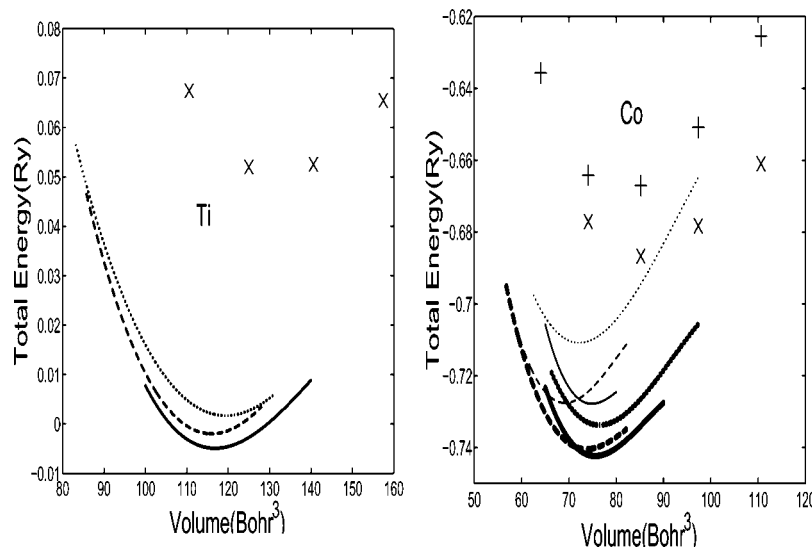

FIG. 6. TB total energies of Ti and Co. The solid line, dotted line, and dashed line represent hcp, bcc, and fcc total energies, respectively. The symbol + denotes simple cubic total energy. In the right graph, the thick lines and thin lines represent ferromagnetic and paramagnetic Co, and the symbols X and + show ferromagnetic and paramagnetic simple cubic, respectively.

TABLE IV. Equilibrium lattice constants and bulk moduli for the experimentally (Ref. 7) observed ground-state structures of the elements, comparing the results of first-principles, and tight-binding parametrization results.

Name	Structure	a(Bohr)			B_0(Mbar)		
		TB	LDA	Expt.	TB	LDA	Expt.
Ca	fcc	9.98	9.96	10.55	0.21	0.13	0.15
V	bcc	5.55	5.54	5.73	2.15	1.96	1.62
Cr	bcc	5.29	5.29	5.44	3.05	3.07	1.90
Fe[a]	bcc	5.38	5.38	5.43	1.76	1.76	1.68
Ni[a]	fcc	6.48	6.48	6.65	2.38	2.52	1.86
Cu	fcc	6.71	6.65	6.82	2.01	1.90	1.37
Sr	fcc	10.94	10.82	11.49	0.11	0.20	0.11
Nb	bcc	6.16	6.16	6.24	1.93	1.95	1.70
Mo	bcc	5.91	5.90	5.95	2.98	2.91	2.72
Rh	fcc	7.11	7.12	7.18	3.87	3.22	2.70
Pd	fcc	7.34	7.29	7.35	1.93	1.84	1.81
Ag	fcc	7.62	7.58	7.73	1.32	1.16	1.01
Ba	bcc	9.02	9.03	9.49	0.17	0.10	0.10
Ta	bcc	6.22	6.12	6.24	2.12	2.24	2.00
W	bcc	5.99	5.94	5.97	3.63	3.33	3.23
Ir	fcc	7.30	7.29	7.26	4.14	3.86	3.55
Pt	fcc	7.43	7.37	7.41	3.34	3.05	2.78
Au	fcc	7.77	7.67	7.71	1.87	1.70	1.73

Name	Structure	a(Bohr)		c(Bohr)		B_0(Mbar)	
		TB	Expt.	TB	Expt.	TB	Expt.
Sc	hcp	5.98	6.25	9.55	9.96	0.34	0.44
Ti	hcp[b]	5.54	5.58	8.81	8.85	1.17	1.05
Co[a]	hcp	4.74	4.74	7.70	7.69	2.35	1.91
Y	hcp	6.58	6.90	10.62	10.83	0.70	0.37
Zr	hcp	5.95	6.11	9.52	9.74	0.87	0.83
Tc	hcp	5.12	5.18	8.38	8.31	5.42	2.97
Ru	hcp	5.10	5.12	7.70	8.09	3.52	3.21
Hf	hcp	6.05	6.03	9.13	9.54	1.06	1.09
Re	hcp	5.21	5.22	8.64	8.43	4.23	3.72
Os	hcp	5.28	5.17	7.61	8.16	6.98	4.18

[a]Ferromagnetic.
[b]hcp lattice fitted.

$$\epsilon_i'(k) = \epsilon_i(k) + V_0. \tag{3}$$

The results of this manipulation is that the first-principles total energy E is given by the expression:

$$E = \Sigma \epsilon_i'(k). \tag{4}$$

We note the constant V_0 is different for each volume and structure of the first-principles database. The reader should recognize that we have shifted each band structure by a constant, retaining the exact shape of the first-principles bands. It should also be stressed that all this is done to the first-principles database before we proceed with the fit that will generate the TB Hamiltonian. In our treatment of ferromagnetic systems the total energy is equal to the sum of spin up and spin down shifted eigenvalues. The difference of these two sums could be viewed as representing the exchange energy.

We write the onsite energies in a polynomial form:

$$h_{il}(\rho_i) = \alpha_l + \beta_l \rho_i^{2/3} + \gamma_l \rho_i^{4/3} + \delta_l \rho_i^2, \tag{5}$$

where l is an angular momentum index, and ρ_i is an atomic-like density that has the form:

$$\rho_i = \sum_{j \neq i} \exp[-\lambda^2 R_{ij}] F_c(R_{ij}), \tag{6}$$

where, R_{ij} is the distance between atom i and j, and F_c is a smooth cutoff function that was used to limit the range of parameters[5]

$$F_c(R) = (1 + e^{(R-R_0)/R_l})^{-1}. \tag{7}$$

We take R_0 to be in the range of $10.0a_0$–$14.0a_0$, and $R_l = 0.5a_0$ (where a_0 is Bohr radius), which effectively zeros all interactions for neighbors more than $14.0a_0$ apart. Typically, depending on the structure and lattice constant, this cutoff function will include 50–80 neighboring atoms.

The parameters λ, α_l, β_l, γ_l, and δ_l are determined by fitting total energies following the NRL-TB procedure as stated above. The hopping parameters were calculated using the modified prefactors of Table I.

We fitted total energies of all transition metals to the APW results[3] at several lattice constants of bcc, fcc, and sc structures. We successfully reproduced the ground state, the order of crystal structures, and the bulk modulus. Our parameters also place the energies of hcp and sc structures, which we did not fit, at reasonable values. As an example, we present energy–volume relationships for four transition metals in Fig. 5, and for the hcp metals Ti and Co in Fig. 6, which again show the correct ordering of crystal structures. We also present in Table IV the equilibrium lattice constants and bulk moduli of transition metals.

An inspection of Table IV reveals that our approach matches very well the LDA lattice constants underestimating the experimental values by 1%–2% for the transition metals and by 4%–5% for the alkaline earths. The bulk moduli have larger deviation from experiment as is usually the case in the LDA. For the hcp metals both the lattice parameters and bulk moduli are also within the LDA predictions except for T_c, O_s, and Y. Those results could be improved if we include the hcp lattice in the fitting database.

IV. CONCLUSION

To recapitulate, we have accomplished two goals. We have reevaluated the ten universal prefactors in Harrison's hopping parameters and redetermined the s, p, d onsite energies together with the parameters γ_s and r_d. This enables us to calculate very accurately the band structure of all the transition, alkaline earth, and noble metals and for the second goal we have used a polynomial form for the onsite energies

which, with the addition of 15 new parameters, provides a total energy capability for our modified Harrison theory.

Finally, we wish to stress that this work constitutes not only an efficient computational method but also a valuable addendum to Harrison's books.

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