Tight-Binding Calculations for d Bands*

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The accurate tight-binding method used by Lafon and Lin has been extended to treat d electrons in transition metals. Formulas to evaluate three-center integrals are presented and applied to the calculation of the $3d$ bands of nickel. Contrary to the usual assumptions in tight-binding calculations for d bands, especially in interpolation or pseudopotential schemes, it is found that the first-neighbor approximation is not adequate to obtain convergence in matrix elements, and that beyond first neighbors the two-center approximation fails badly. Three-center integrals are presented for the first four neighbors and used in a tight-binding calculation for the d bands of nickel. In the following paper, these results are used in a pseudopotential scheme to caclulate energy bands of ferromagnetic nickel.

I. INTRODUCTION

CALCULATIONS of energy bands in transition metals[1] are complicated because of the presence of d electrons which occupy narrow energy bands lying in a broad s-p band. The relative positions of the bands are sensitive to small changes in the crystalline potential and to the form of exchange potential which is used, so self-consistent solutions are needed. However, calculational methods which work well for narrow bands do not for broad ones, and vice versa, and until recently the only method which proved fruitful was the augmented-plane-wave (APW) method.[2] In its usual applications, this method suffers from certain inadequacies, chiefly the muffin-tin potential approximation, which, even in a self-consistent calculation, leaves some uncertainty in the relative position of the d bands and some doubts about the details of the Fermi surface.[3] This approximation is even more serious in transition-metal compounds.[4]

Recent developments which look promising for the transition metals are the combined interpolation schemes developed by Hodges *et al.*[5] and by Mueller,[6] in which d bands are treated by the Slater-Koster[7] form of tight-binding and the s-p bands by the pseudopotential method in a manner similar to Harrison.[8] The parameters in these schemes can be chosen to reproduce accurately first-principles calculations or can be adjusted to obtain agreement with experimental information. One advantage of interpolation schemes

is that computations are quite rapid, permitting a large sampling of points in the Brillouin zone in a reasonable time, for a density-of-states calculation,[3] for example. Another advantage is that inadequacies in the potential used for the first-principles calculation can be compensated conveniently by adjustment of parameters to obtain agreement with experiment. This approach has worked in nickel.[5]

Successful application of interpolation schemes based upon tight-binding expansions for d bands suggest that first-principles tight-binding calculations should be reconsidered. Lack of any good quantitative results in previous tight-binding calculations for transition metals has been difficult to assess, since errors could be due to potentials which were not self-consistent, or to any one of several approximations which are customarily made because of computational difficulties. One of the stronger objections has been that tight-binding functions do not form a complete set of states, and, what may be more important from a practical point of view, do not include any continuum states. These objections have been removed by the work of Lafon and Lin,[9] who applied the tight-binding method to metallic lithium using a potential for which accurate orthogonalized-plane-wave (OPW), augmented-plane-wave (APW), and Green's-function calculations were available. The principal result of their investigation was that the tight-binding method is capable of yielding accurate results, but only if the usual approximations of neglecting three-center integrals and of restricting the sum over neighbors to the first or second neighbors were not made. To do this they carried all sums to convergence and used an accurate method for evaluation of three-center integrals.

In this paper the method of Lafon and Lin is extended to handle d electrons in order to perform more accurate tight-binding calculations for transition metals. In the case of d bands the integrals are substantially more difficult to obtain, but, on the other hand, the sum over neighbors should converge more rapidly. It is expected that the method which worked well for s and p electrons

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[1] J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964).
[2] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).
[3] J. W. D. Connolly, Phys. Rev. **159**, 415 (1967).
[4] J. C. Slater, in *Methods in Computational Physics*, edited by B. Alder, S. Fernback, and M. Rotenberg (Academic Press Inc., New York, 1968), Vol. 8, p. 1.
[5] H. Ehrenreich and L. Hodges, in *Methods in Computational Physics*, edited by B. Alder, S. Fernback, and M. Rotenberg (Academic Press Inc., New York, 1968), Vol. 8, p. 149; L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).
[6] F. M. Mueller, Phys. Rev. **153**, 659 (1967).
[7] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).
[8] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[9] E. E. Lafon and C. C. Lin, Phys. Rev. **152**, 597 (1966).

in lithium will work as well or better for more tightly bound d electrons.

In the paper which immediately follows,[10] results obtained here for d electrons in nickel are combined with a pseudopotential scheme to include s-p conduction bands and hybridization of s-p bands with the d bands.

II. THREE-CENTER INTEGRALS

The basic quantity which must be calculated for d electrons is the three-center integral

$$\langle 3d(\mathbf{A}) | V(\mathbf{r}) | 3d(\mathbf{B}) \rangle,$$

where $3d(\mathbf{A})$ is an atomic orbital centered at site $\mathbf{A}$, and $3d(\mathbf{B})$ is another centered at site $\mathbf{B}$. $V(\mathbf{r})$ is the crystalline potential which leads to three-center integrals, as can be seen most clearly when $V(\mathbf{r})$ is approximated by a superposition of atomic potentials

$$V(\mathbf{r}) = \sum_l V_a(\mathbf{r} - \mathbf{R}_l), \tag{1}$$

where the sum is over all lattice vectors $\mathbf{R}_l$. The integral is conveniently done with a Fourier series expression for the crystalline potential, a form which is not limited to the approximation given by Eq. (1). For crystals with a center of inversion

$$V(\mathbf{r}) = \sum_\nu V(\mathbf{k}_\nu) \cos(\mathbf{k}_\nu \cdot \mathbf{r}_C), \tag{2}$$

where the sum is over all reciprocal-lattice vectors $\mathbf{k}_\nu$, and $\mathbf{r}_C$ is the radius vector measured from any lattice site of the crystal. Integrals with this potential may be done accurately if the atomic orbitals are given in Gaussian form or as sums of Slater-type orbitals (STO). In the latter case the orbital may be Laplace transformed to obtain a Gaussian representation of the wave function. A three-center integral calculated in this way for a $1S$ STO is given in Ref. 9,

$$\langle 1S(\mathbf{A}) | \cos \mathbf{k}_\nu \cdot \mathbf{r}_C | 1S(\mathbf{B}) \rangle = 2\pi\alpha_1\alpha_2 r_{AB}{}^3$$

$$\times \int_0^1 f[3(fg)^{-5/2} + 3(fg)^{-2} + (fg)^{-3/2}]$$

$$\times \exp[-(fg)^{1/2}] \cos(\mathbf{k}_\nu \cdot \mathbf{r}_{CD}) du, \tag{3}$$

where $f = u(1-u)r_{AB}{}^2$, $g = k_\nu{}^2 + \alpha_2{}^2/(1-u) + \alpha_1{}^2/u$, and α_1 and α_2 are the constants which appear in the exponentials for $1S$ orbitals at $\mathbf{A}$ and $\mathbf{B}$, respectively. The variable $\mathbf{r}_{CD}$ is defined by $\mathbf{r}_{CD} = \mathbf{r}_C - \mathbf{r}_D$, where $\mathbf{r}_D$ is the radius vector measured from the point $\mathbf{D}$, which is the point about which is centered a single Gaussian equivalent to the product of the two Gaussians derived from orbitals at the points $\mathbf{A}$ and $\mathbf{B}$. Integrals for orbitals with higher angular momentum or higher principal quantum number can be obtained from the $1s$ integral by partial differentiation with respect to α_1, α_2, A_x, B_x,

etc. For example,

$$\langle 3d_{xy}(\mathbf{A}) | \cos(\mathbf{k}_\nu \cdot \mathbf{r}_C) | 3d_{xy}(\mathbf{B}) \rangle = \frac{\partial}{\partial\alpha_1}\left(\frac{1}{\alpha_1}\frac{\partial}{\partial A_x}\right)$$

$$\times \frac{\partial}{\partial\alpha_1}\left(\frac{1}{\alpha_1}\frac{\partial}{\partial A_y}\right)\frac{\partial}{\partial\alpha_2}\left(\frac{1}{\alpha_2}\frac{\partial}{\partial B_x}\right)\frac{\partial}{\partial\alpha_2}\left(\frac{1}{\alpha_2}\frac{\partial}{\partial B_y}\right)$$

$$\times\langle 1S(\mathbf{A}) | \cos(\mathbf{k}_\nu \cdot \mathbf{r}_C) | 1S(\mathbf{B}) \rangle. \tag{4}$$

These derivatives become quite tedious to work out for d orbitals, since the expressions get lengthy. However, the great advantage is that three-center integrals are reduced to a single one-dimensional integral which can be evaluated simply to the required degree of accuracy. The formulas which are obtained for all the d-d integrals are tabulated in the Appendix to this paper. Kinetic energy integrals may be handled by a similar procedure, but standard programs for doing these two-center integrals are available.[11]

III. APPLICATION TO NICKEL

Formulas given in the Appendix for d electrons have been used to calculate tight-binding matrix elements for nickel. The crystalline potential for nickel was taken as a superposition of spherically averaged atomic potentials constructed to correspond to a $3d^9 4s^1$ configuration. However, wave functions used to construct the potentials were taken from Clementi's calculation[12] for a $3d^8 4s^2$ configuration. For spherically averaged atomic potentials, Fourier coefficients of the crystalline potential depend upon the magnitude of $\mathbf{k}$ only, and in atomic units, are given by

$$V(|\mathbf{k}_\nu|) = -\frac{224\pi}{\Omega_0|\mathbf{k}_\nu|^2} + \frac{8\pi}{\Omega_0|\mathbf{k}_\nu|^3}$$

$$\times\sum_{nl}\int_0^\infty |U_{nl}|^2 \sin(|\mathbf{k}_\nu|r)r\,dr, \tag{5}$$

where U_{nl} are the radial parts of the atomic orbitals multiplied by appropriate occupation numbers and Ω_0 is the volume of the unit cell. The complete Clementi wave function was used in constructing the potential, in forming Bloch sums of atomic orbitals, and in evaluating integrals. The lattice constant for nickel was taken as 6.65454 a.u.

Exchange-potential integrals were calculated separately using a $\rho^{1/3}$ approximation. The charge density in the cell at the origin was obtained by summing the charge due to the first five shells of neighbors. A cubic harmonic expansion of $\rho^{1/3}$ was made and Fourier co-

[10] J. Calloway and H. M. Zhang, following paper, Phys. Rev. B1, 305 (1970).

[11] Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401

[12] E. Clementi, *Tables of Atomic Functions* (IBM Corp., San Jose, 1965).

TABLE I. Independent three-center integrals. Column 3, kinetic plus potential energy; column 4, Slater exchange potential; column 5, overlap integrals.

Integral	Neighbor	KE+PE (Ry)	Exchange (Ry)	Overlap
xy, xy	000	3.068580	−3.813905	1.0000
$3z^2-r^2, 3z^2-r^2$	000	3.071944	−3.811621	1.0000
xy, xy	110	−0.011861	−0.024091	0.016737
xy, xy	101	0.0095334	0.0078754	−0.0061056
xy, xz	011	0.013563	0.012076	−0.0092478
x^2-y^2, x^2-y^2	110	0.022098	0.018289	−0.015353
$3z^2-r^2, 3z^2-r^2$	110	−0.0060100	−0.010101	0.0076737
$xy, 3z^2-r^2$	110	0.0049848	0.011641	−0.0078489
xy, xy	200	0.0021099	0.0026407	−0.0020257
xy, xy	002	−0.00036745	−0.00032069	0.00027525
x^2-y^2, x^2-y^2	002	−0.00074436	−0.00043323	0.00027525
$3z^2-r^2, 3z^2-r^2$	002	−0.0041559	−0.0044223	0.0043343
xy, xy	211	−0.00043833	−0.00026864	0.00022428
xy, xy	112	−0.00013124	−0.000038024	0.000033202
xy, xz	211	−0.00086815	−0.00066016	0.00047039
xy, xz	112	−0.00020191	−0.00015190	0.00012739
x^2-y^2, x^2-y^2	112	0.00017601	0.00016703	−0.00010236
$3z^2-r^2, 3z^2-r^2$	112	−0.00030271	−0.000037912	0.000016849
$xy, 3z^2-r^2$	112	−0.00028109	−0.00034960	0.00031779
$xy, 3z^2-r^2$	211	0.000046395	0.000041325	−0.000068827
$yz, 3z^2-r^2$	112	−0.00051831	−0.00045745	−0.00015890
xy, xy	220	−0.00069908	−0.00036740	0.00023502
xy, xy	202	0.0000032347	0.000048957	−0.000041662
xy, xz	022	0.0000222188	0.000059859	−0.000049807
x^2-y^2, x^2-y^2	220	0.000019317	0.00010167	−0.000091470
$3z^2-r^2, 3z^2-r^2$	220	−0.00023901	−0.00012394	0.000083771
$xy, 3z^2-r^2$	220	0.00039125	0.00020253	−0.00013099

efficients evaluated by integrating over the Wigner-Seitz sphere. Nonspherical components were then dropped for convenience, since they were found to contribute less than 1% to the total.

Matrix elements needed for the tight-binding method can be written[7]

$$H_{nm}(\mathbf{k}) = \sum (\mathbf{R}_j) \exp(i\mathbf{k} \cdot \mathbf{R}_j) E_{nm}(\mathbf{R}_j), \qquad (6)$$

with

$$E_{nm}(\mathbf{R}_j) = \int \varphi_n^*(\mathbf{r}) H \varphi_m(\mathbf{r}-\mathbf{R}_j) dv, \qquad (7)$$

where φ_n and φ_m are the atomic orbitals. The overlap matrix is

$$S_{nm} = \sum (\mathbf{R}_j) \exp(i\mathbf{k} \cdot \mathbf{R}_j) \int \varphi_n^*(\mathbf{r}) \varphi_m(\mathbf{r}-\mathbf{R}_j) dv,$$

and the secular equation is

$$\det |H_{ij} - E S_{ij}| = 0.$$

The number of independent E integrals can be greatly reduced by symmetry consideration. From group theory it follows that, for example,

$$E_{xy,x^2-y^2}(abc) = \tfrac{1}{2} E_{xy,x^2-y^2}(cba) + \tfrac{3}{2} E_{xy,3z^2-r^2}(cba), \qquad (8)$$

which is a relation between an integral with d functions transforming like xy located at the origin and d functions transforming like x^2-y^2 or $3z^2-r^2$ at the points (abc) or (cba). Coefficients multiplying the integrals on the right of Eq. (8) are determined by transformation

properties of d functions under an operation of the cubic group which takes point (abc) to (cba). Similar equations hold for other operations and other types of integrals, so that for the first four neighbors there are only 27 independent potential integrals.

Integrals needed for forming matrix elements in the tight-binding method are given in Table I for the first four neighbors. Integrals for the potential given by Eq. (5) plus the kinetic energy are listed in column 3, while the Slater exchange-potential integrals are given in column 4, and overlap integrals in column 5.

It is sometimes desirable to adjust the form of the exchange potential by choosing a different over-all numerical factor; for example, multiplying by $\tfrac{2}{3}$ to get the Kohn-Sham form.[13] This can be accomplished simply by introducing a factor λ to the exchange-potential integrals as they are added to kinetic and Coulomb integrals to form matrix elements. Unless otherwise stated, results quoted in this paper were obtained for $\lambda = 0.85$, a value suggested in Ref. 10.

A common approximation found in tight-binding calculations is neglect of three-center terms appearing in (7). The energy integrals can then be written in the two-center approximation in terms of atomic orbital two-center integrals[7] $(dd\sigma)$, $(dd\pi)$, and $(dd\delta)$. Relations given in Ref. 7 may be solved simultaneously to yield these two-center integrals from the three-center results given in Table I, but, depending upon which relations are used, different values are obtained. A measure of

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[13] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

Table II. Two-center integral equivalents for first neighbors.

Two-center parameter	KE+PE (Ry)	Mean (Ry)	Exchange (Ry)	Mean (Ry)	Overlap
$dd\sigma$	−0.01479	−0.01469	−0.03109	−0.03054	0.02127
	−0.01464		−0.03026		
	−0.01464		−0.03026		
$dd\pi$	0.02215	0.02231	0.01829	0.01874	−0.01535
	0.02210		0.01886		
	0.02310		0.01995		
	0.02210		0.01829		
	0.02210		0.01829		
$dd\delta$	−0.003085	−0.003345	−0.003106	−0.003517	0.003142
	−0.004030		−0.004201		
	−0.003132		−0.003380		
	−0.003132		−0.003380		

validity of the two-center approximations is the variation of these results. This is shown in Table II for the first-neighbor integrals for several of the relations. Overlap integrals are two-center integrals, so the same result is obtained for each set of relations. Evidently, the two-center approximation is valid to about 5–10% for first neighbors, with the greatest variations occurring for the $(dd\delta)$ integral. Mean values of two-center integrals for first neighbors are compared in Table III with the values calculated by Fletcher and Wohlfarth,[14] Hodges et al.,[5] and Zornberg.[15] The Fletcher-Wohlfarth parameters have been corrected by a factor of $\frac{1}{2}\pi$ as suggested by Allan et al.,[16] and mean values of Hodges' two-center integrals are listed. The Fletcher integrals were calculated directly using a model muffin-tin potential and copper wave functions, while Hodges' and Zornberg's integrals were obtained from three-center and two-center fits to APW calculations, respectively.

For second and third neighbors, the two-center approximation fails badly: Variations of the integrals by factors of about 5 are found, so that no approximately consistent set could be obtained.

For first neighbors the three-center integrals obtained from this calculation may be compared with three-center parameters obtained by fitting[5] an APW calculation[17] and by fitting a Green's-function calculation.[18]

This is done for the six independent first-neighbor integrals in Table IV, using a factor of $\lambda = 0.85$ in the exchange potential. Three-center integrals from the present work are consistently higher than the parameter values, the largest discrepancy occurring for the $x^2 - y^2$ integral. Aside from differences in crystal potentials for the calculations, discrepancies could be expected due to the fitting procedure, which neglected overlap integrals and included only first neighbors in calculating matrix elements.

Errors produced by neglecting contributions from other neighbors can produce substantial changes in the band structure, or, conversely, cause changes in parameters fit to bands which include more neighbors implicitly. This is clearly evident in Fig. 1, where a portion of the d bands of nickel are shown in the first-neighbor (broken lines) and fourth-neighbor (solid lines) approximation. While the fourth-neighbor bands are convergent to less than 0.005 Ry, there are qualitative differences in going from first to fourth neighbors: relative positions of levels X_1 and X_3 are interchanged, causing a crossing of bands along Δ, and the separation of levels X_2 and X_5 changes substantially, although the order remains the same. For the potential given by

Table III. Comparison of two-center integrals for first neighbors.

	$\lambda = 0$ (Ry)	$\lambda = 0.85$ (Ry)	Fletcher[a] (Ry)	Hodges[b] (Ry)	Zornberg[c] (Ry)
$(dd\sigma)_1$	−0.01469	−0.04065	−0.0390	−0.0384	−0.038
$(dd\pi)_1$	0.02231	0.03824	0.0210	0.0228	0.0173
$(dd\delta)_1$	−0.00335	−0.00633	−0.0030	−0.00565	−0.0017

[a] Corrected by factor of $\frac{1}{2}\pi$ (Ref. 16).
[b] From three-center fit to APW calculation (Ref. 5).
[c] From two-center fit to APW calculation (Ref. 15).

Table IV. Comparison of three-center integrals for first neighbors.

	Present work (Ry)	Hodges et al.[a] (Ry)	Wakoh[b] (Ry)
$E_{xy,xy}(110)$	−0.03234	−0.03037	−0.02643
$E_{xy,xy}(011)$	0.01623	0.00899	0.00766
$E_{xy,xz}(011)$	0.02271	0.01559	0.01504
$E_{x^2-y^2,x^2-y^2}(110)$	0.03764	0.02091	0.02495
$E_{3z^2-r^2,3z^2-r^2}(110)$	−0.01460	−0.01248	−0.01271
$E_{xy,3z^2-r^2}(110)$	0.01488	0.01421	0.01649

[a] Reference 5.
[b] Reference 18.

[14] G. C. Fletcher and E. P. Wohlfarth, Phil. Mag. 42, 106 (1951).
[15] E. I. Zornberg, Phys. Rev. B1, 244 (1970).
[16] G. Allan, W. M. Lomer, R. D. Lowde, and C. G. Windsor, Phys. Rev. Letters 20, 933 (1968).

[17] J. G. Hanus, M.I.T. Solid State and Molecular Theory Group Quarterly Progress Report No. 44, p. 29, 1962 (unpublished).
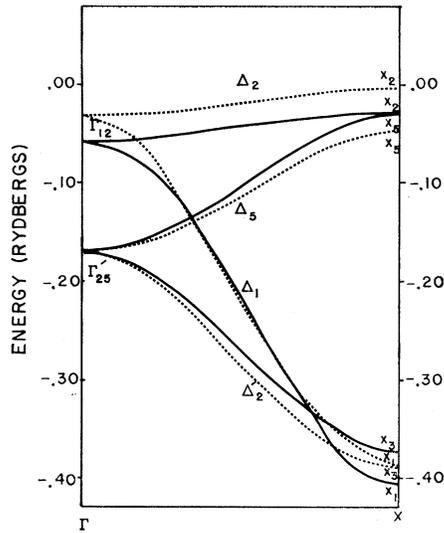[18] S. Wakoh and T. Yamashita, J. Phys. Soc. Japan 19, 1342 (1964).

FIG. 1. Energy bands along Δ axis. Broken lines are first-neighbor approximation; solid lines are fourth-neighbor approximation. Exchange parameter $\lambda=0.85$.
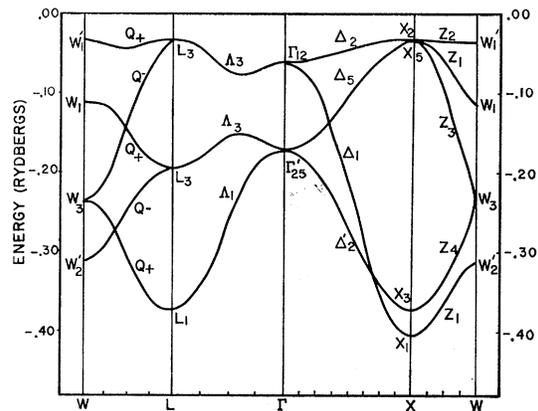

FIG. 2. Energy bands along symmetry axes. Exchange parameter $\lambda=0.85$. Matrix elements summed to convergence.

Eq. (5) and with the exchange parameter $\lambda=0.85$, the order obtained for X_5 and X_2 is reversed from that obtained in previous calculations[2,17,19] for paramagnetic nickel. This order is sensitive to the crystal field splitting

$$\Delta E = E_{xy,xy}(000) - E_{x^2-y^2,x^2-y^2}(000) ,$$

and may be in error because of the form of the crystal potential, a superposition of spherically symmetric potentials. This question could best be resolved by a self-consistent calculation, not restricted to this form.

The band structure along several lines of symmetry is shown in Fig. 2 for $\lambda=0.85$. The d band width is calculated to be 0.377 Ry, which may be compared with 0.304 Ry for Ref. 19, and 0.37 Ry for Ref. 17. The major qualitative difference from previous calculations is the position of the X_5 level.

IV. CONCLUSION

The three-center integrals given in the Appendix have been used to calculate energy bands for a potential constructed to represent paramagnetic nickel. Although the potential was a superposition of spherically averaged atomic potentials, formulas in the Appendix are not limited to this form, nor are they limited to a muffin-tin form. In performing the band calculation, special attention was paid to approximations involved, but no attempt at a complete first-principles calculation for nickel was made. Conclusions drawn are: (1) The first-neighbor approximation is inadequate for accurate tight-binding matrix elements for the d bands, (2) convergence in tight-binding matrix elements is obtained

after third or fourth neighbors, (3) the two-center approximation is valid to about 5–10% for first neighbors, but not justified for other neighbors.

These conclusions, of course, do not invalidate a pseudopotential scheme based upon one of these approximations, but give an indication of the accuracy which might be obtained from such a calculation, and qualify interpretation (in terms of first-principle results) of parameters obtained from a fitting procedure.

One of the problems with combined pseudopotential schemes, especially for ferromagnetic-band calculations, is the large number of parameters which enter the calculations to fit only a limited amount of data. In addition to tight-binding parameters, there are pseudopotential, orthogonalization, and hybridization coefficients, spin-splitting factors and the spin-orbit parameter needed to obtain detailed agreement with experiment, for example, Fermi-surface data. It is suggested[10] that the d-band part of these combined pseudopotential schemes could be treated by first principles, using the results of this paper and a reasonable potential to eliminate d-band parameters, while treating the remaining interactions as before. This would have the advantage of reducing the number of free parameters while increasing accuracy of the d bands. In addition, the pseudopotential scheme would not depend on a fit to another first-principles calculation (APW, for example), but could evolve independently, relying only upon experimental data as in the usual psuedopotential methods.[8] This approach is used in Ref. 10 to calculate the band structure, spin splitting, and spin-wave effective mass in nickel.

[19] J. Yamashita, M. Fukuchi, and S. Wakoh, J. Phys. Soc. Japan **18**, 999 (1963).

APPENDIX

Expressions of the type given by Eq. (4) are presented in this Appendix. In addition to the definitions made in Sec. II of this paper, the following are convenient:

$$A_1 = f\left(\frac{3}{(fg)^{5/2}} + \frac{3}{(fg)^2} + \frac{1}{(fg)^{3/2}}\right),$$

$$A_2 = f^2\left(\frac{15}{(fg)^{7/2}} + \frac{15}{(fg)^3} + \frac{6}{(fg)^{5/2}} + \frac{1}{(fg)^2}\right),$$

$$A_3 = f^3\left(\frac{105}{(fg)^{9/2}} + \frac{105}{(fg)^4} + \frac{45}{(fg)^{7/2}} + \frac{10}{(fg)^3} + \frac{1}{(fg)^{5/2}}\right),$$

$$A_4 = f^4\left(\frac{945}{(fg)^{11/2}} + \frac{945}{(fg)^5} + \frac{420}{(fg)^{9/2}} + \frac{105}{(fg)^4} + \frac{15}{(fg)^{7/2}} + \frac{1}{(fg)^3}\right),$$

$$A_5 = f^5\left(\frac{10395}{(fg)^{13/2}} + \frac{10395}{(fg)^6} + \frac{4725}{(fg)^{11/2}} + \frac{1260}{(fg)^5} + \frac{210}{(fg)^{9/2}} + \frac{21}{(fg)^4} + \frac{1}{(fg)^{7/2}}\right),$$

$$B_x - A_x = D_x, \qquad\qquad\qquad (\mathbf{K}_\nu)_x = K_x,$$

$$B_y - A_y = D_y, \qquad\qquad\qquad (\mathbf{K}_\nu)_y = K_y,$$

$$B_z - A_z = D_z, \qquad\qquad\qquad (\mathbf{K}_\nu)_z = K_z,$$

$$h = u(1-u).$$

In terms of these quantities, unnormalized three-center integrals for $3d$ Slater-type orbitals become

$$\langle 3d_{xy}(\mathbf{A}) | \cos\mathbf{K}_\nu \cdot \mathbf{r}_C | 3d_{xy}(\mathbf{B})\rangle = 2\pi\alpha_1\alpha_2 r_{AB}{}^3 \int_0^1 \llbracket D_x{}^2 D_y{}^2 h^2 \cos\mathbf{K}_\nu \cdot \mathbf{r}_{CD} A_1$$

$$+ [-(D_y{}^2 + D_x{}^2)\cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) + (K_x D_x D_y{}^2 + K_y D_x{}^2 D_y)(1-2u)\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})]hA_2$$

$$+ \{[K_y K_x D_x D_y(-1+4u-4u^2) + hK_x{}^2 D_y{}^2 + hD_x{}^2 K_y{}^2 + 1]\cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) + (2u-1)(K_y D_y + K_x D_x)\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})\}A_3$$

$$+ [-(K_x{}^2 + K_y{}^2)\cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) + (K_x{}^2 K_y D_y + K_x K_y{}^2 D_x)(1-2u)\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})]A_4$$

$$+ K_x{}^2 K_y{}^2 \cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) A_5\rrbracket e^{-(fg)^{1/2}} du,$$

$$\langle 3d_{xy}(\mathbf{A}) | \cos\mathbf{K}_\nu \cdot \mathbf{r}_C | 3d_{yz}(\mathbf{B})\rangle = 2\pi\alpha_1\alpha_2 r_{AB}{}^3 \int_0^1 \llbracket D_y{}^2 D_z D_x \cos\mathbf{K}_\nu \cdot \mathbf{r}_{CD}\, h^2 A_1$$

$$+ \{-D_z D_x \cos\mathbf{K}_\nu \cdot \mathbf{r}_{CD} + [D_y{}^2((1-u)K_z D_x - D_z u K_x) + D_y D_z D_x(1-2u)K_y]\sin\mathbf{K}_\nu \cdot \mathbf{r}_{CD}\}hA_2$$

$$+ \{[h(K_y K_z D_x D_y + K_y{}^2 D_z D_x + K_z K_x D_y{}^2 + K_y K_x D_z D_y) + K_y D_y(-K_z D_x(1-u)^2 - K_x D_z u^2)]\cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})$$

$$+ [-K_z D_x(1-u) + D_z K_x u]\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})\}A_3$$

$$+ \{[(1-u)K_y K_z(K_y D_x + K_x D_y) - u K_y K_x(K_z D_y + K_y D_z)]\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) - K_x K_z \cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})\}A_4$$

$$+ K_z K_x K_y{}^2 \cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) A_5\rrbracket e^{-(fg)^{1/2}} du,$$

$$\langle 3d_{xy}(\mathbf{A}) | \cos\mathbf{K}_\nu \cdot \mathbf{r}_C | 3d_{x^2-y^2}(\mathbf{B})\rangle = 2\pi\alpha_1\alpha_2 r_{AB}{}^3 \int_0^1 \{(D_x{}^3 D_y - D_y{}^3 D_x)\cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})\, h^2 A_1$$

$$+ [(K_x D_x{}^2 D_y - K_y D_y{}^2 D_x)(2-3u) - (D_x{}^3 K_y - D_y{}^3 K_x)u]\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})\, hA_2$$

$$+ [((K_x{}^2 - K_y{}^2)D_x D_y(1-u)(3u-1) + (D_x{}^2 - D_y{}^2)K_x K_y u(2-3u))\cos(\mathbf{K}_\nu \cdot \mathbf{r}_{CD}) + 2(K_y D_x - K_x D_y)\sin(\mathbf{K}_\nu \cdot \mathbf{r}_{CD})]A_3$$

$$+[((K_x{}^3D_y-K_y{}^3D_x)(1-u)+(K_x{}^2K_yD_x-K_y{}^2K_xD_y)(1-3u))\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})]A_4$$

$$+(K_x{}^3K_y-K_y{}^3K_x)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_5\}e^{-(fg)^{1/2}}du\,,$$

$$\langle 3d_{x^2-y^2}(\mathbf{A})\,|\cos(\mathbf{K}_\nu\cdot\mathbf{r}_C|\,3d_{x^2-y^2}(\mathbf{B})\rangle=2\pi\alpha_1\alpha_2 r_{AB}{}^3\int_0^1\{(D_x{}^2-D_y{}^2)^2\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,h^2A_1$$

$$+[-4(D_x{}^2+D_y{}^2)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+(K_xD_xD_y{}^2+K_yD_yD_x{}^2-D_x{}^3K_x-D_y{}^3K_y)2(2u-1)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})]hA_2$$

$$+[4(2u-1)(K_xD_x+K_yD_y)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+(-(6u^2-6u+1)(K_x{}^2D_x{}^2+K_y{}^2D_y{}^2)+(1-2u+2u^2)$$

$$\times(K_y{}^2D_x{}^2+K_x{}^2D_y{}^2)-8hK_xK_yD_xD_y+4)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})]A_3$$

$$+[2(2u-1)(-K_x{}^3D_x-K_y{}^3D_y+K_y{}^2K_xD_x+K_yK_x{}^2D_y)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})-4(K_x{}^2+K_y{}^2)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})]A_4$$

$$+(K_x{}^2-K_y{}^2)^2\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_5\}e^{-(fg)^{1/2}}du\,,$$

$$\langle 3d_{yz}(\mathbf{A})\,|\cos(\mathbf{K}_\nu\cdot\mathbf{r}_C|\,3d_{x^2-y^2}(\mathbf{B})\rangle=2\pi\alpha_1\alpha_2 r_{AB}{}^3\int_0^1\big[D_yD_z(D_x{}^2-D_y{}^2)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,h^2A_1$$

$$+\{[2(1-u)D_yD_z(K_xD_x-K_yD_y)+u(D_y{}^2-D_x{}^2)(K_yD_z+K_zD_y)]\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+2D_yD_z\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}hA_2$$

$$+\{[2(1-u)K_yD_z-2uK_zD_y]\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[-(1-u)^2D_yD_z(-K_y{}^2+K_x{}^2)+2h(K_xK_yD_xD_z+K_zK_xD_xD_y$$

$$-K_y{}^2D_yD_z)-K_zK_y(u^2D_x{}^2+u(2(1-u)-u)D_y{}^2)]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_3$$

$$+\{[(1-u)K_x{}^2(K_yD_z+K_zD_y)+(1-u)K_y{}^2(-K_zD_y-K_yD_z)-2uK_zK_y(K_xD_x-K_yD_y)]\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})$$

$$+2K_yK_z\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_4$$

$$+(K_x{}^2K_yK_z-K_y{}^3K_z)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_5\big]e^{-(fg)^{1/2}}du\,,$$

$$\langle 3d_{xy}(\mathbf{A})\,|\cos(\mathbf{K}_\nu\cdot\mathbf{r}_C)|\,3d_{3z^2-r^2}(\mathbf{B})\rangle=6\pi\alpha_1\alpha_2 r_{AB}{}^3\int_0^1\Big\{D_z{}^2D_yD_x\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,h^2A_1$$

$$+\{[2(1-u)-h]D_yD_x\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[2K_zD_zD_yD_x(1-u)-uD_z{}^2(D_xK_y+K_xD_y)]h\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_2$$

$$+\{(D_xK_y+K_xD_y)(u-2)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[-K_z{}^2D_yD_x(1-u)^2+2K_zD_zK_yD_xh+2K_xK_zD_zD_yh-K_xK_yD_z{}^2u^2$$

$$-\tfrac{1}{3}\alpha_2{}^2D_xD_y]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_3$$

$$+\Big[\frac{u-2}{1-u}K_yK_x\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+\Big((1-u)K_z{}^2(K_yD_x+K_xD_y)-2uK_xK_zK_yD_z+\frac{\alpha_2{}^2}{3(1-u)}(K_xD_y+K_yD_x)\Big)$$

$$\times\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\Big]A_4$$

$$+\Big(K_z{}^2K_yK_x+\frac{\alpha_2{}^2K_xK_y}{3(1-u)^2}\Big)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_5\Big\}e^{-(fg)^{1/2}}du\,,$$

$$\langle 3d_{zx}(\mathbf{A})\,|\cos(\mathbf{K}_\nu\cdot\mathbf{r}_C)|\,3d_{3z^2-r^2}(B)\rangle=6\pi\alpha_1\alpha_2 r_{AB}{}^3\int_0^1\Big\{D_z{}^3D_x\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})h^2A_1$$

$$+\{[(2-3u)hK_zD_z{}^2D_x-uhD_z{}^3K_x]\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[-3h+2(1-u)]D_zD_x\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_2$$

$$+\{[(3u-4)K_zD_x+(3u-2)K_xD_z]\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[K_z{}^2D_zD_x(1-u)(3u-1)+u(2-3u)K_zK_xD_z{}^2$$

$$-\tfrac{1}{3}\alpha_2{}^2D_zD_x]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_3$$

$$+\Big[\frac{K_zK_x(3u-4)}{(1-u)}\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+\Big(K_z{}^3D_x(1-u)-K_z{}^2K_xD_z(3u-1)+\frac{\alpha_2{}^2}{3(1-u)}(K_zD_x+K_xD_z)\Big)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\Big]A_4$$

$$+\left(K_z{}^3K_x+\frac{\alpha_2{}^2K_zK_x}{3(1-u)^2}\right)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_5\bigg\}e^{-(fg)^{1/2}}du\,,$$

$$\langle 3d_{3z^2-r^2}(\mathbf{A})\,|\cos(\mathbf{K}_\nu\cdot\mathbf{r}_C)\,|\,3d_{3z^2-r^2}(\mathbf{B})\rangle=18\pi\alpha_1\alpha_2 r_{AB}{}^3\int_0^1\bigg\{D_z{}^4h^2\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_1$$

$$+[-2(2u-1)hD_z{}^3K_z\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+(2-6h)D_z{}^2\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})]A_2$$

$$+\{6(2u-1)D_zK_z\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[-(6u^2-6u+1)K_z{}^2D_z{}^2-\tfrac{1}{3}D_z{}^2(\alpha_1{}^2+\alpha_2{}^2)+3+2/h]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_3$$

$$+\bigg[\bigg[2(1-2u)K_z{}^3D_z+2/3K_zD_z\bigg(\frac{\alpha_2{}^2}{1-u}-\frac{\alpha_1{}^2}{u}\bigg)\bigg]\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+\bigg[(6u^2-6u-1)K_z{}^2-\frac{2}{3}\bigg(\frac{\alpha_1{}^2}{u}+\frac{\alpha_2{}^2}{1-u}\bigg)$$

$$+\frac{\alpha_1{}^2+\alpha_2{}^2}{3}\bigg]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})/h\bigg]A_4$$

$$+\bigg(K_z{}^4+\frac{\alpha_2{}^2K_z{}^2}{3(1-u)^2}+\frac{\alpha_1{}^2K_z{}^2}{3u^2}+\frac{\alpha_1{}^2\alpha_2{}^2}{9h^2}\bigg)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\,A_5\bigg\}e^{-(fg)^{1/2}}du\,,$$

$$\langle 3d_{x^2-y^2}(\mathbf{A})\,|\cos(\mathbf{K}_\nu\cdot\mathbf{r}_C)\,|\,3d_{3z^2-r^2}(\mathbf{B})\rangle=6\pi\alpha_1\alpha_2 r_{AB}{}^3\int_0^1\bigg\{D_z{}^2(D_x{}^2-D_y{}^2)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})h^2A_1$$

$$+\{[2(1-u)(D_x{}^2-D_y{}^2)+h(D_y{}^2-D_x{}^2)]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+[(1-u)K_zD_z(D_x{}^2-D_y{}^2)+uD_z{}^2(K_yD_y-K_xD_x)]2h$$

$$\times\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_2$$

$$+\{(4-2u)(K_yD_y-K_xD_x)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})+\tfrac{1}{3}\alpha_2{}^2D_y{}^2+(1-u)^2K_z{}^2(D_y{}^2-D_x{}^2)+u^2D_z{}^2(K_y{}^2-K_x{}^2)-\tfrac{1}{3}\alpha_2{}^2D_x{}^2$$

$$+4hK_zD_z(K_xD_x-K_yD_y)]\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\}A_3$$

$$+\bigg[\bigg(2K_z{}^2(1-u)(K_xD_x-K_yD_y)+2uK_z(K_y{}^2D_z-K_x{}^2D_z)+\frac{2}{3}\frac{\alpha_2{}^2}{1-u}(K_xD_x-K_yD_y)\bigg)\sin(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})$$

$$+\bigg(\frac{u}{1-u}(K_x{}^2-K_y{}^2)+\frac{2}{1-u}(K_y{}^2-K_x{}^2)\bigg)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})\bigg]A_4$$

$$+\bigg(K_z{}^2K_x{}^2+\frac{\alpha_2{}^2K_x{}^2}{3(1-u)^2}-K_z{}^2K_y{}^2-\frac{K_y{}^2\alpha_2{}^2}{3(1-u)^2}\bigg)\cos(\mathbf{K}_\nu\cdot\mathbf{r}_{CD})A_5\bigg\}e^{-(fg)^{1/2}}du\,.$$