

## Shifts in the Electronic Band Structure of Metals Due to Non-Muffin-Tin Potentials\*

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The generally neglected potential outside the muffin-tin spheres induces average energy shifts of the order of 0.005 to 0.010 Ry in fully relativistic, high-symmetry levels of fcc palladium, fcc platinum, and bcc uranium. The high band mass of these transition metals combined with such shifts can cause errors of the order of 5% in predicting the Fermi radii. The splitting of the spin-orbit doublets is found to be insensitive to the inclusion of the outside of the muffin-tin potential. By augmenting a phase-shift parameter set with two or three effective pseudopotential coefficients which represent the effect of the weak added potential, an *ab initio* band structure may be used to fit accurate experimental data.

## I. INTRODUCTION

MANY calculations of the electronic band structure of materials have utilized the muffin-tin approximation to the one-electron potential. First introduced by Slater in his 1947 paper on the augmented-plane-wave (APW) method,<sup>1</sup> this approximation offers several simplifying features in carrying out the numerical calculations.<sup>2</sup> The crystal potential, which is constructed by taking a superposition of spherically averaged free-atom charge densities from the neighboring atoms, is made spherically symmetric within a sphere about each atomic site. It is taken to be constant (flat) between the APW spheres and is found<sup>3-5</sup> from the requirements (a) that the unit cell be neutral and (b) that the Coulomb potentials integrate to the sum of the atomic Coulomb potentials. The muffin-tin potential can be treated as containing a number of adjustable parameters. Quite aside from the choice of atomic configuration and state of ionization (an important question for ionic compounds) assumed in the atomic calculations used to obtain the free atom charge densities, one can vary the radii of the APW muffin tins and the potential between the spheres. Used as a semiempirical method to fit certain experimental features of the band structure, this parametrization scheme can lead to some improvement in the results obtained.<sup>6</sup> It is not, however, a general

technique—nor a satisfying procedure to carry out from an *ab initio* point of view.

For those metals which have many tightly bound core electrons and only a few, nearly free conduction electrons, viz., the simple and noble metals, the muffin-tin approximation has been found to be adequate, as expected. For covalently bonded semiconductors and semimetals, the muffin-tin approximation is rather inadequate,<sup>5-11</sup> and the corrections introduced by the non-flat potential outside the muffin-tin spheres can cause substantial shifts in selected energy levels. For the intermediate case of the transition and actinide metals, the effect of the muffin-tin approximation has not been studied and is not well known.

In this paper we include the variations of the potential outside the muffin-tin sphere into relativistic APW calculations and show for the case of transition and actinide metals<sup>12</sup>—specifically, fcc palladium, fcc platinum, and bcc uranium—the resultant corrections which are introduced into the calculated energy bands.

## II. THEORY

The symmetrized relativistic APW method (SRAPW)<sup>5</sup> has been used to calculate band structures

<sup>1</sup> P. DeCicco, Phys. Rev. **153**, 931 (1967).

<sup>2</sup> A. R. Williams, Phys. Letters **25A**, 75 (1967); F. Beleznyay and M. J. Lawrence, J. Phys. C. **1**, 1288 (1968); B. Segall, Phys. Rev. **124**, 1797 (1961); R. S. Leigh, Proc. Phys. Soc. (London) **71**, 33 (1957).

<sup>3</sup> R. Sandrock, in Proceedings of the First International Symposium on the Physics of Selenium and Tellurium, Montreal, 1967 (to be published).

<sup>4</sup> A. B. Kunz, W. B. Folwer, and P. M. Schneider, Phys. Letters **28A**, 553 (1969).

<sup>5</sup> W. Rudge, Phys. Rev. **181**, 1020 (1969); **181**, 1024 (1969).

<sup>6</sup> The standard muffin-tin SRAPW calculations on Pd have not been reported by us previously. Preliminary results have been reported for Pt [A. J. Freeman and D. D. Koelling, Bull. Am. Phys. Soc. **14**, 28 (1969)], and for U [A. J. Freeman and D. D. Koelling, *ibid.* **14**, 360 (1969)].

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<sup>1</sup> J. C. Slater, Phys. Rev. **51**, 846 (1937).

<sup>2</sup> T. L. Loucks, *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967), and references therein.

<sup>3</sup> For a discussion of the muffin-tin prescription, see F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

<sup>4</sup> L. F. Matthiess, Phys. Rev. **133**, 184 (1963); **134**, A1399 (1964).

<sup>5</sup> D. D. Koelling (to be published).

<sup>6</sup> P. Scop, Phys. Rev. **139**, A934 (1965).

for all three metals. Briefly, this technique is similar to the APW<sup>1</sup> and RAPW<sup>2</sup> methods, but uses double-space-group projection operators to greatly reduce the effective size of the plane-wave basis set. This enables one to obtain better convergence for an equal rank secular matrix than one could obtain with the unsymmetrized RAPW method and to automatically identify eigenfunction character. In addition, several improvements in numerical procedure have been introduced.<sup>5</sup>

The potential for an APW calculation divides itself naturally into two parts: one inside and one outside the muffin-tin radius. If one follows the prescription for the model potential of overlapping free-atom potentials and charge densities—for which the method of Mattheiss<sup>4</sup> yields the muffin-tin approximation—three contributions must be considered. The largest contribution is made by the strong core charge density centered inside the muffin-tin sphere on a single ion. It is treated exactly within the APW sphere. Next in importance is the overlapping charge density from a neighboring ion which falls inside a Wigner-Seitz cell. (It is treated approximately as a spherical average within the APW sphere.) The exchange and correlation effects are the weakest. These are included approximately within the SRAPW method in terms of the Slater free-electron approximation,  $\alpha C\rho^{1/3}$ , where  $\alpha$  is treated as a disposable parameter.

Normally within the APW method, the model potential is spherically averaged within the muffin-tin spheres and replaced by a constant outside the spheres (the “muffin-tin floor”). This constant potential is determined<sup>3-5</sup> (generally analytically) so that one has charge neutrality and the correct average Coulomb potential—consistent with the model chosen. In practice, it is convenient to move the zero of energy so that it lies at the muffin-tin floor.

TABLE I. Fourier coefficients for fcc palladium potential outside muffin-tin spheres derived from an atomic configuration  $4d^{10}6s^0$  with full Slater exchange ( $\alpha=1$ ) in Rydberg units.

Star	1 term	11 terms	19 terms
1	0.0045	-0.8695	-0.8332
2		-3.0092	-2.8457
3		-1.5555	-1.4538
4		-0.7404	-0.6550
5		-0.5141	-0.4276
6		-0.1064	-0.0869
7		-0.0392	-0.0350
8		-0.0023	-0.0029
9		-0.0163	-0.0093
10		-0.0255	-0.0205
11		-0.0085	-0.0106
12			0.0010
13			0.0007
14			-0.0002
15			0.0000
16			0.0014
17			0.0000
18			0.0001
19			0.0000
rms error of fit	0.08420	0.00007	0.00003

TABLE II. Fourier coefficients for fcc platinum potential outside muffin-tin spheres derived from an atomic configuration  $5d^{10}6s^0$  with full Slater exchange ( $\alpha=1$ ) Rydberg units.

Star	19 terms	11 terms	6 terms	5 terms	1 term
1	-0.8613	-0.9346	-0.8885	-0.7414	0.0039
2	-2.8715	-3.2171	-2.9911	-2.4038	
3	-1.4195	-1.6371	-1.4963	-1.1539	
4	-0.5211	-0.7219	-0.5796	-0.3434	
5	-0.2443	-0.4639	-0.3075	-0.1314	
6	-0.0359	-0.0912	-0.0434		
7	-0.0061	-0.0337			
8	-0.0033	-0.0030			
9	0.0092	-0.0104			
10	0.0042	-0.0205			
11	-0.0054	-0.0091			
12	0.0005				
13	0.0008				
14	0.0029				
15	-0.0004				
16	0.0014				
17	0.0000				
18	0.0001				
19	0.0000				
rms error of fit	0.00004	0.00010	0.00047	0.00198	0.10520

To investigate the effects of a more general potential, it is useful to write the potential<sup>7</sup> as

$$V(\mathbf{r}) = V_{\text{MT}}(\mathbf{r}) + V_1(\mathbf{r}) + V_2(\mathbf{r}), \quad (1)$$

where  $V_1$  and  $V_2$  denote the difference between the potential  $V$  and its muffin-tin approximation  $V_{\text{MT}}$ . This difference has been broken into two parts by requiring  $V_1$  to be nonzero only outside the muffin-tin spheres and  $V_2$  to be nonzero only inside the spheres. This is done because it is appropriate to expand these two quantities differently— $V_1$  as a Fourier series and  $V_2$  in spherical harmonics. Furthermore, since the effects of  $V_1$  should be much larger<sup>13</sup> than the effects of  $V_2$ , it is possible to consider the inclusion of  $V_1$  alone. This intermediate approximation will be denoted as the warped muffin-tin (WMT). Because the basis functions are plane wave in the region where  $V_1$  is nonzero, the WMT approximation only requires augmentation of the muffin-tin secular equation with the Fourier components of  $V_1$ ,

$$\langle \mathbf{k}s | H^{\text{WMT}} - E | \mathbf{k}'s' \rangle = \langle \mathbf{k}s | H^{\text{MT}} - E | \mathbf{k}'s' \rangle + \langle s | s' \rangle V_1(\mathbf{k}' - \mathbf{k}). \quad (2)$$

(Note that this is not perturbation theory.) The WMT approximation will be used in the calculations on the high- $Z$  fcc and bcc crystals.

In this work the potential outside the spheres is Fourier analyzed by a two-step process. First, the potential in this outside region is least-squares fit using the  $\Gamma_1$  harmonics

$$s(\mathbf{K}_n, \mathbf{r}) = - \frac{1}{g} \sum_{\alpha} e^{i\alpha \mathbf{K}_n \cdot \mathbf{r}} u(\mathbf{r}), \quad (3)$$

<sup>13</sup> J. C. Slater and P. DeCicco, Q. P. R., Solid State and Molecular Theory Group, M. I. T. October 15, 1963, p. 46 (unpublished).

TABLE III. Fourier coefficients for fcc platinum potential outside muffin-tin spheres derived from an atomic configuration  $5d^{10}6s^0$  with  $\frac{2}{3}$  Slater exchange in Rydberg units.

Star	19 terms	11 terms	6 terms	5 terms	4 terms	3 terms	1 term
1	-0.9671	-0.9314	-0.7608	-0.6200	-0.5250	-0.3620	-0.0017
2	-3.4741	-3.2973	-2.5289	-1.9666	-1.6159	-1.0731	
3	-1.8201	-1.7079	-1.2355	-0.9078	-0.7038	-0.4123	
4	-0.9866	-0.8725	-0.4654	-0.2393	-0.1252		
5	-0.7856	-0.6529	-0.2427	-0.0742			
6	-0.1867	-0.1493	-0.0416				
7	-0.0709	-0.0437					
8	-0.0019	-0.0006					
9	-0.0406	-0.0283					
10	-0.0508	-0.0297					
11	-0.0142	-0.0056					
12	0.0003						
13	0.0002						
14	0.0035						
15	0.0001						
16	0.0003						
17	0.0000						
18	0.0000						
19	0.0000						
rms error of fit	0.00001	0.00003	0.00041	0.00190	0.00443	0.01240	0.10100

where  $\mathbf{K}_n$  is a reciprocal lattice vector and the sum of the operations  $\alpha$  ranges over all  $g$  (here 48) operations of the point group of the symmorphic crystal.  $u(\mathbf{r})$  is a step function defined to be zero inside the spheres and unity outside the spheres.

The expansion coefficients  $C_n$  for the potential  $V_1$  are given by

$$V_1(\mathbf{r}) = \sum_n C_n s(\mathbf{K}_n, \mathbf{r}). \quad (4)$$

Initially, the  $C_n$ 's were obtained using approximately 250 random points in the region outside the spheres. Note that within a Monte Carlo approach this procedure for finding  $C_n$ 's is equivalent to a Fourier transform analysis, but is rather easier to carry out numerically. However, because there are no points used inside the muffin-tin spheres, in effect, we have not defined

the function Eq. (4) in this region. Thus, even though convergence is obtained, the expansion obtained will not be completely defined and the coefficients will vary greatly with the inclusion of more harmonics. Tables I-IV show this variation. If this fit to the outside region is then reanalyzed with the requirement on  $V_1$  that the function vanish in the interior of the muffin-tin spheres,

$$V_1(\mathbf{K}) = \frac{1}{g} \sum_n C_n \sum_{\alpha} U(\mathbf{K} + \alpha \mathbf{K}_n), \quad (5)$$

$$U(\mathbf{K}) = \delta_{\mathbf{K},0} - \frac{4\pi R_s^3}{\Omega} \frac{j_1(KR_s)}{KR_s},$$

TABLE V. Matrix elements for palladium potential of Table I for fcc lattice. Here  $A$  ( $n$ ) means  $A \times 10^n$ .TABLE IV. Fourier coefficients for bcc uranium derived from an atomic configuration using  $\frac{2}{3}$  Slater exchange ( $7s^2 6d^5 f^3$ ) in Rydberg units.

Star	1 term	6 terms	11 terms	16 terms
1	0.0036	-0.7933	-1.0515	-1.1459
2		-3.7795	-5.4965	-6.2119
3		-0.5152	-0.9734	-1.1950
4		-0.5734	-1.5157	-2.0604
5		-0.0732	-0.2984	-0.4621
6		-0.0343	-0.2391	-0.4271
7			-0.0345	-0.0675
8			-0.0614	-0.1839
9			-0.0022	-0.0095
10			-0.0019	-0.0174
11			-0.0008	-0.0096
12				-0.0079
13				-0.0036
14				-0.0013
15				-0.0011
16				-0.0003
rms error of fit	0.09100	0.00068	0.00002	0.00001

Star	$\mathbf{K}$ vector	11 terms	19 terms
3	(4,0,0)	0.9866 (-2)	0.9867 (-2)
4	(4,4,0)	0.4348 (-2)	0.4348 (-2)
6	(4,4,4)	0.6181 (-3)	0.6178 (-3)
8	(8,0,0)	-0.2464 (-3)	-0.2472 (-3)
10	(8,4,0)	0.5437 (-3)	0.5440 (-3)
11	(8,4,4)	0.1561 (-2)	0.1560 (-2)
13	(12,0,0)	-0.1863 (-2)	-0.1864 (-2)
14	(8,8,0)	0.4533 (-3)	0.4523 (-3)
15	(8,8,4)	-0.1161 (-2)	-0.1161 (-2)
17	(12,4,0)	-0.1370 (-2)	-0.1369 (-2)
18	(12,4,4)	-0.4928 (-3)	-0.4944 (-3)
20	(8,8,8)	0.4630 (-3)	0.4651 (-3)
1	(0,0,0)	0.1629 (-3)	-0.4630 (-3)
2	(2,2,2)	-0.6274 (-2)	-0.6275 (-2)
5	(6,2,2)	-0.4042 (-2)	-0.4042 (-2)
7	(6,6,2)	-0.1702 (-3)	-0.1698 (-3)
9	(6,6,6)	0.5475 (-3)	0.5471 (-3)
12	(10,2,2)	0.1758 (-2)	0.1758 (-2)
16	(10,6,2)	-0.7048 (-3)	-0.7048 (-3)
19	(10,6,6)	-0.5814 (-3)	-0.5805 (-3)
21	(10,10,2)	0.3874 (-3)	0.3891 (-3)
22	(10,10,6)	0.8042 (-3)	0.7997 (-3)
23	(10,10,10)	-0.7079 (-3)	-0.7060 (-3)

the coefficients rapidly stabilize with the inclusion of more and more  $\Gamma_1$  harmonics in the fit. Tables IV–VIII show the stabilization. In Eq. (5),  $U(\mathbf{k})$  is the Fourier transform of the unit step function (zero inside the spheres and one outside);  $\Omega$  is the volume of the unit cell; and  $R_s$  is the radius of the muffin-tin sphere. The stability of  $V_1(\mathbf{K})$  is far more important than the stability of the  $C_n$  since  $V_1(\mathbf{K})$  appears in the matrix elements.

### III. RESULTS

Tables I–IV present values of the coefficients in the Fourier function expansions for the WMT potential, Eq. (1). They were derived by the least-squares procedure above for fcc palladium ( $\alpha=1$  or full Slater free-electron exchange), fcc platinum ( $\alpha=1$ ), fcc platinum ( $\alpha=\frac{2}{3}$ ), and bcc uranium ( $\alpha=1$ ), respectively. In all four cases the convergence and absolute error of the fit suggest that 15–18 stars form an adequate representation of the WMT potential. The atomiclike  $d$  states are slightly more extended in the case of the  $\alpha=\frac{2}{3}$  exchange than in the case of the full Slater exchange. Therefore the WMT coefficients for  $\alpha=\frac{2}{3}$  are larger, term by term, than the WMT coefficients for  $\alpha=1$  in the converged 18-term-fit representation.

Tables V–VIII present the matrix elements of the four cases of WMT potentials whose coefficients were given in Tables I–IV, respectively. The important point to notice is that the actual matrix elements entering the SRAPW secular equation have much better convergence properties than the Fourier expansion coefficients alone—a very useful result since the matrix element is the actual quantity affecting the results. This follows from the fact that the step function  $U$  present in the definition of  $V_1(\mathbf{r})$  is now being represented within the Fourier series removing the uncertainty in the coefficients.

Tables IX–XI present the actual shifts in energy of selected high-symmetry levels induced by the WMT potentials for the four cases considered. Because of the symmetry of the eigenfunctions, individual energy

TABLE VI. Matrix elements for platinum potential of Table II for simple-cubic and bcc vectors. Here  $A(n)$  means  $A \times 10^n$ .

$K$ vector	19 terms	11 terms	6 terms
Simple cubic			
(0,0,0)	0.6121 (−4)	0.6081 (−4)	0.5232 (−4)
(4,0,0)	0.1221 (−1)	0.1221 (−1)	0.1220 (−1)
(4,4,0)	0.5852 (−2)	0.5853 (−2)	0.5850 (−2)
(4,4,4)	−0.3683 (−4)	−0.3672 (−4)	−0.3781 (−4)
(8,0,0)	−0.1108 (−2)	−0.1107 (−2)	−0.1121 (−2)
(8,4,0)	0.5341 (−3)	0.5338 (−3)	0.5472 (−3)
Body-centered cubic			
$K$ vector	19 terms	11 terms	6 terms
(2,2,2)	−0.8033 (−2)	−0.8033 (−2)	−0.8027 (−2)
(6,2,2)	−0.4795 (−2)	−0.4795 (−2)	−0.4793 (−2)
(6,6,2)	−0.3351 (−3)	−0.3355 (−3)	−0.3365 (−3)
(6,6,6)	0.1123 (−2)	0.1124 (−2)	0.1169 (−2)

eigenvalues shift by rather large amounts (of the order of 0.01 Ry), whereas other states, at the same point in the Brillouin zone, do not shift at all. Note also that the shifts induced by the WMT may be either positive or negative in sign. To clarify the nature of these induced shifts, we define four types of averages of the energy levels of Tables IX–XI. The first is the simple average shift defined as

$$\Delta E = \frac{1}{N_i} \sum_{n, \mathbf{k}_i} [E_n(\mathbf{k}) - E_n^0(\mathbf{k})], \quad (6)$$

where the sum over  $n$  and  $\mathbf{k}_i$  is carried out over all the points  $\mathbf{k}_i$  or levels  $n$  given in the tables,  $E_n^0(\mathbf{k})$  are the levels without the WMT,  $E_n(\mathbf{k})$  with the WMT, and  $N_i$  is the total number of points and levels. We see from the tables that the average shift, Eq. (6), is, in fact, very small for the metals considered. We believe that this is due to the fact that the zero of energy of the muffin-tin potential (the muffin-tin floor) is exactly the same as the zero of energy of the warped muffin tin. Thus the average shift between the energy bands for the two cases would involve essentially second-order differences.

TABLE VII. Matrix element for platinum potential of Table III for simple-cubic and bcc vectors. Here  $A(n)$  means  $A \times 10^n$ .

$K$ vector	11 terms	6 terms	5 terms	4 terms	3 terms
Simple cubic					
(0,0,0)	−0.1785 (−2)	−0.1784 (−2)	−0.1785 (−2)	−0.1898 (−2)	−0.1773 (−2)
(4,0,0)	0.1237 (−1)	0.1237 (−1)	0.1239 (−1)	0.1236 (−1)	0.1233 (−1)
(4,4,0)	0.4974 (−2)	0.4973 (−2)	0.4996 (−2)	0.4988 (−2)	0.5383 (−2)
(4,4,4)	0.5703 (−4)	0.5642 (−4)	0.7542 (−4)	−0.2552 (−3)	0.1123 (−3)
(8,0,0)	−0.1122 (−2)	−0.1113 (−2)	−0.1181 (−2)	−0.1266 (−2)	0.1373 (−3)
(8,4,0)	0.6240 (−3)	0.6105 (−3)	0.6953 (−3)	0.5657 (−3)	0.7065 (−3)
Body-centered cubic					
$K$ vector	11 terms	6 terms	5 terms	4 terms	3 terms
(2,2,2)	−0.7354 (−2)	−0.7353 (−2)	−0.7367 (−2)	−0.7317 (−2)	−0.7344 (−2)
(6,2,2)	−0.4680 (−2)	−0.4678 (−2)	−0.4696 (−2)	−0.4619 (−2)	−0.5201 (−2)
(6,6,2)	0.2142 (−4)	0.2517 (−4)	−0.3501 (−4)	0.1426 (−3)	0.2876 (−3)
(6,6,6)	0.9129 (−3)	0.9171 (−3)	0.9548 (−3)	0.1019 (−2)	0.7674 (−3)

TABLE VIII. Matrix element for uranium potential of Table IV for bcc lattice. Here  $A$  ( $n$ ) means  $A \times 10^n$ .

Star	$K$ vector	6 terms	11 terms	16 terms
1	(0,0,0)	0.4106 (-3)	0.3991 (-3)	0.3991 (-3)
2	(2,2,0)	-0.2251 (-2)	-0.2248 (-2)	-0.2248 (-2)
3	(4,0,0)	0.1000 (-1)	0.1000 (-1)	0.1000 (-1)
4	(4,2,2)	0.4420 (-3)	0.4414 (-3)	0.4414 (-3)
5	(4,4,0)	-0.1849 (-2)	-0.1849 (-2)	-0.1848 (-2)
6	(6,2,0)	-0.4392 (-2)	-0.4392 (-2)	-0.4392 (-2)
7	(4,4,4)	-0.1910 (-2)	-0.1943 (-2)	-0.1943 (-2)
8	(6,4,2)	0.2005 (-2)	0.2019 (-2)	0.2019 (-2)
9	(8,0,0)	0.4548 (-2)	0.4548 (-2)	0.4548 (-2)
10	(6,6,0)	0.1031 (-2)	0.9919 (-3)	0.9919 (-3)
11	(8,2,2)	0.2180 (-2)	0.2163 (-2)	0.2163 (-2)
12	(8,4,0)	-0.1511 (-3)	-0.1437 (-3)	-0.1438 (-3)
13	(6,6,4)	-0.8087 (-3)	-0.8041 (-3)	-0.8043 (-3)
14	(8,4,4)	-0.1073 (-2)	-0.1082 (-2)	-0.1082 (-2)
15	(8,6,2)	-0.1472 (-2)	-0.1463 (-2)	-0.1463 (-2)
16	(10,4,2)	-0.5617 (-3)	-0.5638 (-3)	-0.5639 (-3)
17	(8,8,0)	0.5044 (-3)	0.5077 (-3)	0.5075 (-3)
18	(8,6,6)	0.1028 (-2)	0.1027 (-2)	0.1027 (-2)
19	(8,4,4)	-0.1073 (-2)	-0.1082 (-2)	-0.1082 (-2)
20	(10,6,4)	0.8436 (-3)	0.8421 (-3)	0.8420 (-3)
21	(12,4,0)	0.1089 (-2)	0.1086 (-2)	0.1086 (-2)
22	(10,8,2)	0.5208 (-3)	0.5206 (-3)	0.5205 (-3)
23	(12,4,4)	0.1725 (-3)	0.1829 (-3)	0.1831 (-3)
24	(12,6,2)	-0.1183 (-3)	-0.1132 (-3)	-0.1134 (-3)
25	(8,8,8)	-0.1063 (-2)	-0.1060 (-2)	-0.1060 (-2)
26	(10,2,0)	-0.1873 (-2)	-0.1857 (-2)	-0.1857 (-2)
27	(10,6,0)	0.9209 (-3)	0.9141 (-3)	0.9145 (-3)
28	(12,0,0)	0.5022 (-3)	0.4751 (-3)	0.4752 (-3)
29	(12,2,2)	0.9795 (-3)	0.9695 (-3)	0.9697 (-3)

The second type of average corresponds to the rms deviation of individual levels away from the average shift. The square of the second average is defined as

$$\sigma^2 = \Delta E^2 = \frac{1}{N_i \sum_{n, \mathbf{k}_i} [E_n(\mathbf{k}) - E_n^0(\mathbf{k})]^2} - (\Delta E)^2. \quad (7)$$

TABLE IX. Selected high-symmetry levels for fcc  $4d^{10}5s^0$  full Slater exchange ( $\alpha=1$ ) palladium with and without the outside muffin-tin potential in Rydberg units.

Level	WMT	Muffin-tin	Difference
$\Gamma_6^+$	-0.0014	-0.0007	-0.0007
$\Gamma_8^+$	0.2830	0.2854	-0.0024
$\Gamma_7^+$	0.3073	0.3098	-0.0025
$\Gamma_8^+$	0.4034	0.4044	-0.0010
$X_6^+$	0.1102	0.1055	-0.0047
$X_7^+$	0.1356	0.1403	-0.0047
$X_7^+$	0.4793	0.4794	-0.0002
$X_6^+$	0.5030	0.5032	-0.0002
$X_7^+$	0.5246	0.5248	-0.0002
$X_6^-$	0.7691	0.7803	-0.0112
$L_6^+$	0.1242	0.1296	-0.0054
$L_4^+$	0.2734	0.2749	-0.0015
$L_6^+$	0.2994	0.3009	-0.0015
$L_6^+$	0.4809	0.4811	-0.0002
$L_4^+$	0.4954	0.4956	-0.0002
$L_6^-$	0.5958	0.5892	0.0066
$W_7$	0.1851	0.1805	0.0046
$W_6$	0.2525	0.2564	-0.0039
$W_7$	0.2627	0.2667	-0.0040
$W_6$	0.3967	0.3973	-0.0006
$W_7$	0.5123	0.5125	-0.0002

$$\Delta E = -0.0016$$

$$\sigma = 0.0034$$

$$\Delta E_{sd} = 0.0006$$

$$\sigma_{sd} = 0.0073$$

The rms deviation of the shifts  $\sigma$  is actually more significant than the simple average since  $\sigma$  would enter, for example, as an effective broadening of the density of states. The rms deviation is smallest in the case of palladium, and largest for uranium with platinum for  $\alpha=1$  and  $\alpha=\frac{2}{3}$  intermediate. This increasing sensitivity to the WMT terms for heavier metals is consistent with the increased softening and broadening of the  $d$  and  $f$  resonances with higher  $Z$  and higher number of core levels. Again, it should be noted that the energy levels derived for platinum in the case with  $\alpha=\frac{2}{3}$  are more sensitive to the WMT potential than the full Slater ( $\alpha=1$ ) case. The effective  $5d$  radius of the former is larger than in the latter case.

For the fcc metals, where the separation between  $d$ -like states and plane-wave like states is rather clear, we define two more averages which test the relative sensitivity of the  $s$  or  $d$  levels to the WMT. The first such  $s$ - $d$  average shift is defined as

$$\Delta E_{sd} = \frac{1}{N_d} \sum_{i=d, \mathbf{k}} [E_i(\mathbf{k}) - E_i^0(\mathbf{k})] - \frac{1}{N_s} \sum_{j=s, \mathbf{k}} [E_j(\mathbf{k}) - E_j^0(\mathbf{k})], \quad (8)$$

where the sum on  $j$  is carried out over the “ $s$ -like” levels,  $\Gamma_6^+$ ,  $X_6^-$ , and  $L_6^-$ , and the sum on  $i$  over the “ $d$ -like” levels at the points  $\Gamma$ ,  $X$  and  $L$ ;  $N_d$  is the number of  $d$  levels, and  $N_s$ , the number of  $s$  levels. Again the  $E_i(\mathbf{k})$  levels are the warped muffin tin, and the  $E_i^0(\mathbf{k})$  are the muffin-tin levels as before. The surprising result of our analysis is that the net  $s$ - $d$  shift  $\Delta E_{sd}$ , in both palladium and platinum, is very nearly zero. We conjecture that the relative insensitivity exhibited here is due to the fact that the muffin-tin potential used has been defined so that the unit cell average potential is the same as that for the model potential.<sup>3</sup> Thus, any net  $s$ - $d$  shift would involve essentially second-order differences.

At individual  $k$ -space points, however, a substantial  $s$ - $d$  shift can exist. We test for such a dispersive shift by defining a root-mean-square deviation,  $\sigma_{sd}$ , analogous with Eq. (7). We give

$$\sigma_{sd}^2 = \frac{1}{N_k} \sum_{\mathbf{k}} \left( \frac{1}{N_d} \sum_{i=d} [E_i(\mathbf{k}) - E_i^0(\mathbf{k})] - \frac{1}{N_s} \sum_{j=s} [E_j(\mathbf{k}) - E_j^0(\mathbf{k})] \right)^2 - (\Delta E_{sd})^2, \quad (9)$$

where  $N_k$  is the number of  $\mathbf{k}$  points used (here 3), and the sum on  $\mathbf{k}$  is taken over the points  $\Gamma$ ,  $X$ , and  $L$ . For the three cases considered, the value of  $\sigma_{sd}$  is of the order of 0.01 Ry.

Although we have not explicitly carried out a factorization of the levels of bcc uranium because of complications due to the increased hybridization of the

TABLE X. Selected high-symmetry levels for fcc  $5d^{10}6s^0$  full and  $\frac{2}{3}$ -full Slater exchange platinum with and without the outside muffin-tin potential in Rydberg units.

Level	WMT	$\alpha=1$ Muffin-tin	Difference	WMT	$\alpha=\frac{2}{3}$ Muffin-tin	Difference	
$\Gamma_6^+$	-0.0992	-0.0977	-0.0015	-0.0422	-0.0391	-0.0031	
$\Gamma_8^+$	0.3274	0.3314	-0.0040	0.5015	0.5065	-0.0050	
$\Gamma_7^+$	0.4040	0.4087	-0.0047	0.5682	0.5738	-0.0056	
$\Gamma_8^+$	0.5252	0.5274	-0.0022	0.7142	0.7167	-0.0025	
$X_6^+$	0.1196	0.1127	0.0069	0.2332	0.2255	0.0077	
$X_7^+$	0.1595	0.1667	-0.0072	0.2958	0.3045	-0.0087	
$X_7^+$	0.6115	0.6118	-0.0003	0.8229	0.8233	-0.0004	
$X_6^+$	0.6387	0.6389	-0.0002	0.8550	0.8555	-0.0005	
$X_7^+$	0.7106	0.7110	-0.0004	0.9240	0.9246	-0.0006	
$X_6^-$	0.7645	0.7779	-0.0134	0.8291	0.8450	-0.0159	
$L_6^+$	0.1101	0.1183	-0.0082	0.2183	0.2287	-0.0104	
$L_4^+$	0.3129	0.3155	-0.0026	0.4825	0.4857	-0.0032	
$L_6^+$	0.3892	0.3918	-0.0026	0.5495	0.5527	-0.0032	
$L_6^-$	0.6028	0.5940	0.0088	0.6600	0.6525	0.0075	
$L_6^+$	0.6095	0.6102	-0.0007	0.8198	0.8206	-0.0008	
$L_4^+$	0.6582	0.6584	-0.0002	0.8658	0.8661	-0.0003	
$W_7$	0.2171	0.2099	0.0072	0.3438	0.3346	-0.0008	
$W_6$	0.2926	0.2971	-0.0050	0.4413	0.4490	-0.0077	
$W_7$	0.3159	0.3213	0.0046	0.4475	0.4565	0.0010	
$W_6$	0.4936	0.4953	-0.0017	0.6601	0.6613	-0.0012	
$W_7$	0.6683	0.6683	0.0000	0.8841	0.8835	0.0006	
$\Delta E = -0.0014$ $\sigma = 0.0050$		$\Delta E_{sd} = 0.0001$ $\sigma_{sd} = 0.0102$		$\Delta E = -0.0027$ $\sigma = 0.0051$		$\Delta E_{sd} = -0.0011$ $\sigma_{sd} = 0.0109$	

various  $s$ ,  $p$ ,  $d$ , and  $f$  symmetry types, it is clear from Table XI that in this case as well one could expect dispersive shifts of the order of 0.01 Ry.

In the fcc lattice, the triply degenerate  $\Gamma_{25'}$  and doubly degenerate  $X_5$  and  $L_3$  single group,  $d$ -like representations, become in the double-group representation, the levels  $\Gamma_8^+$  and  $\Gamma_7^+$ ,  $X_6^+$  and  $X_7^+$ , and  $L_4^+$  and  $L_6^+$ , respectively. The degeneracy of each of these levels is lifted by spin-orbit coupling<sup>14</sup> between atomiclike  $d$  states. From the tables it is clear that each of these levels shifts by exactly the same amount as its single group mate. Alternatively one can say that the net spin-orbit interaction between these levels is unaffected by the WMT terms. This is consistent with the picture that the greatest strength of the spin-orbit interaction occurs at short radius, i.e., far inside the muffin-tin sphere radius.

#### IV. CONCLUSION AND DISCUSSION

In this paper we have considered the effect of the non-muffin-tin part of the one-electron potential on the electronic band structure of three different metals, two crystallographic structures, and full ( $\alpha=1$ ) and partial ( $\alpha=\frac{2}{3}$ ) Slater exchange. We find, for the cases considered, that the neglected terms induce net shifts of the order of 0.005–0.010 Ry. Since these shifts are substantial, it is essential to include the WMT terms, Eq. (5), in calculating transition and actinide metal band structures. Particularly significant is the fact that levels of completely  $d$ -like character also have net shifts rela-

tive to the  $s$ -like levels of the same order of magnitude, since such shifts can change critical point structure, i.e., change the density of states. Since the effective masses of transition metal bands can be of the order of 10, energy shifts of the order of 0.01 Ry could induce inaccuracies in predicting Fermi radii of the order of 5% of a half-Brillouin-zone distance. Thus, if one wishes to derive effective scattering potentials from accurate experimental data, it is essential to include the WMT terms.

TABLE XI. Selected high-symmetry levels for bcc  $7s^26d^45f^3$  uranium with (WMT) and without the outside the muffin-tin potential in Rydberg units.

State	WMT	Muffin-tin	Difference
$\Gamma_6^+$	0.5809	0.5750	0.0059
$\Gamma_7^-$	1.0065	1.0052	0.0013
$\Gamma_8^-$	1.0138	1.0125	0.0013
$\Gamma_8^+$	1.0883	1.1036	-0.0153
$\Gamma_7^+$	1.1282	1.1443	-0.0161
$\Gamma_8^-$	1.3085	1.3065	0.0020
$\Gamma_6^-$	1.3397	1.3403	-0.0006
$\Gamma_8^+$	1.3540	1.3419	0.0129
$H_8^+$	0.5622	0.5528	0.0094
$H_7^-$	1.1023	1.1094	-0.0071
$H_6^-$	1.1626	1.1647	-0.0026
$H_8^-$	1.1905	1.1911	-0.0006
$H_7^-$	1.3458	1.3463	-0.0005
$H_8^-$	1.3621	1.3625	-0.0004
$P_{6/7}$	1.1513	1.1575	-0.0062
$P_8$	1.1555	1.1506	0.0049
$P_8$	1.2140	1.2178	-0.0038
$P_{6/7}$	1.2416	1.2437	-0.0021
$P_8$	1.2579	1.2750	-0.0171
$\Delta E = -0.0023$		$\sigma = 0.0079$	

<sup>14</sup> F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdyna (to be published).

The rapid convergence of the matrix elements, Tables V–VIII, for all three metals suggests that it is sufficient to find the first few terms of the WMT expansion, Eq. (5), and set the rest of the terms equal to zero. This simplification is of little practical value in calculating band structures including the WMT terms from *ab initio* potentials since it is about as easy and quick to include many terms in Eq. (5) in the matrix elements as a few, provided a sufficient number are used.

The real value of the rapid convergence is in using the band structure to simulate experimental data. Here we consider de Haas–van Alphen (dHvA) Fermi-surface data, which restricts our discussion to states on or very near the Fermi energy shell. In terms of effective one-electron muffin-tin potentials, such states are wholly determined by the energy-dependent phase shifts (or logarithmic derivatives) at the muffin-tin sphere radius. For states at the Fermi energy, this means that the effects of the strong core potential over all  $\mathbf{k}$  space may be given in terms of just a few phase shifts, and these may be treated as disposable parameters for fitting experimental data.

Fermi radii can be obtained from dHvA measurements to an accuracy of the order of  $\frac{1}{2}\%$ . Assuming an average band mass of the order of 2–3, this means that the effective experimental error in  $E_F$ , the Fermi energy, given by this experiment is of the order of 0.003 Ry for the metals considered here. Thus the WMT terms, which induce changes of the order of 0.005–0.010 Ry must be included in order to meaningfully compare theoretical predictions with experimental data.

If one wishes to derive effective scattering potentials—phase shifts—from experimental data, then the WMT terms must be included in the variational scheme in order not to distort the phase shifts by the effects of the

WMT terms. The simplest means of accomplishing this is to augment the parameter set representing the inside the muffin-tin spheres potential as either energy-dependent phase shifts or logarithmic derivatives by a set representing the WMT potential itself, i.e., augment the parameter set by the coefficients of the Fourier series, Eq. (5). Since in all four cases examined in the paper the WMT terms were found to be small, one may treat these terms as being derived from an effective pseudopotential.<sup>15</sup> Moreover, since the matrix elements, Eq. (2), were actually rather insensitive to the number of stars used, Table VII suggests that perhaps two or three adjustable parameters are sufficient to adequately represent the WMT potential.

Still left unanswered is the question of the uniqueness of the separation of the effective scattering potential into phase shifts and WMT terms. Clearly, the result is unique if one proceeds from calculated charge densities to potentials to band structures, as in the SRAPW method. Whether the inverse is also true cannot be stated at this time, although the small size of the WMT terms suggests that if we use a perturbation argument, the value of the WMT terms, but perhaps not the signs, can be determined uniquely. We hope to return to this topic in a future publication.

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<sup>15</sup> W. A. Harrison, *The Pseudopotential Method* (W. A. Benjamin, Inc., New York, 1966), and references therein.