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## THE OVERLAP OF ELECTRON CORE STATES FOR VERY HIGH COMPRESSIONS

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### I. INTRODUCTION

At normal density and for modest compressions, the electronic structure of a metal can be accurately described by treating the conduction electrons and their interactions with the usual methods of band theory. The core electrons remain essentially the same as for an isolated free atom and do not participate in the bonding forces responsible for creating a condensed phase. As the density increases, the core electrons begin to "see" one another as the overlap of the tails of wave functions can no longer be neglected. The electronic structure of the core electrons is responsible for an effective repulsive interaction that eventually becomes free-electron-like at very high compressions.

The electronic structure of the interacting core electrons may be treated in a simple manner using the Atomic Surface Method (ASM).<sup>1</sup> The ASM is a first-principles treatment of the electronic structure involving a rigorous integration of the Schrödinger equation within the atomic-sphere approximation.<sup>2</sup> Solid phase wave functions are constructed from isolated atom wave functions and the band width  $W_i$  and the center of gravity of the band  $C_i$  are obtained from simple formulas. The ASM can also utilize analytic forms of the atomic wave functions and thus provide direct functional dependence of various aspects of the electronic structure. Of particular use in understanding the behavior of the core electrons, the ASM provides the analytic density dependence of the band widths and positions.

The Atomic Surface Method is discussed in Sec. II with a complete derivation and applications to transition metals and f-shell metals given in Ref. 1.

The process whereby core states interact with one another is best viewed as the formation of narrow electron bands formed from atomic states. As the core-core overlap increases, the bands increase in width and mean energy. In Sec. III this picture is further developed and from the ASM one obtains the analytic dependence on density of the relative motion of the different bands. Also in Sec. III is a discussion of the transition to free-electron bands. As an example, the results for the 3s, 3p, and 3d core states and their evolution into bands for nickel are given.

## II. THE ATOMIC SURFACE METHOD FOR ELECTRONIC STRUCTURE

It is now possible to make a simple calculation of the electronic structure for overlapping core orbitals using the Atomic Surface Method (ASM).<sup>1</sup> The ASM is a first-principles treatment of the electronic structure that is computationally simple and can provide immediate analytic dependence of the principal band quantities. The theory has been derived in detail in Ref. 1, and only the main results of the theory will be presented here.

The ASM makes use of the properties of linear combinations of atomic orbitals (LCAO) wave functions. The theory can be roughly characterized in three main steps. The first step consists of using the atomic-sphere approximation<sup>2</sup> and a rigorous integration of the radial Schrödinger equation for the  $l$ th orbital to obtain an exact expression for the bandwidth  $W_l$  in terms of the condensed phase wave function evaluated at the atomic sphere radius  $r_0$ . Next, the condensed phase wave function is constructed in terms of the wave functions of an isolated atom. This then allows one to use analytic forms for atomic wave functions that are accurate in the asymptotic regions and which remain valid in the solid even for large compressions. The final step consists of writing the position of the band center  $C_l$  in terms of the overlap integrals from adjacent sites using once again LCAO results and the atomic sphere approximation. A complete description of the electronic structure is obtained with the Friedel model<sup>3</sup> for the density of states  $n_l(E)$ .

The result for the band width is

$$W_l = \frac{-\hbar^2}{m} \frac{A_0}{N} \left. \frac{\partial p(r)}{\partial r} \right|_{r_0} \quad (II.1)$$

N is the normalization integral equal to

$$N = \int_0^{r_0} 4\pi r^2 \rho_l(r) dr \quad , \quad (II.2)$$

and is near unity at the zero pressure density. N departs significantly from one only at extremely high compressions. The position for the center of gravity is given by

$$C_l = \epsilon_l + 1/2 S_l W_l = \epsilon_l + \rho_0 \rho_l W_l \quad , \quad (II.3)$$

where  $S_l = 2\rho_l \rho_0$  is the overlap integral.  $\rho_0$  is the atomic sphere volume equal to  $4\pi r_0^3/3$  and  $A_0$  is the surface area of the atomic sphere equal to  $4\pi r_0^2$ . The Friedel model for the density of states is

$$n_l = \frac{2(2l+1)}{W_l} \quad \text{for} \quad C_l - \frac{1}{2} W_l < E < C_l + \frac{1}{2} W_l \quad , \quad (II.4)$$

and zero otherwise.

As expressed above, the entire problem of describing the electronic structure has been reduced to finding the wavefunction and its first derivative at a single position, the atomic sphere radius  $r_0$ . In addition, at  $r_0$  the wave function has been expressed in terms of the wave function of an isolated atom and may be evaluated from the Hartree-Fock tables of Mann.<sup>5</sup> This procedure has worked remarkably well for the transition-metal and f-shell-metal systems and the results are contained in Ref. 1. We will now proceed to the use of analytic expressions for the atomic wave functions.

At sufficiently large distances, the potential in the Hartree-Fock calculation of the electronic structure of a neutral atom approaches  $-e^2/r$ . The asymptotic form of the solution of the radial Schrodinger equation is given by

$$R_l(r) \sim r^\gamma e^{-\mu r} \quad , \quad (II.5)$$

where the exponential coefficient is related to the atomic term value  $\epsilon$  by

$$-\epsilon = \hbar^2 \mu^2 / 2m \quad , \quad (II.6)$$

and

$$\gamma = e^2 m / \hbar^2 \mu - 1 \quad . \quad (II.7)$$

For  $-\epsilon=1$  Ry,  $\gamma$  is identically zero. We set  $\gamma=0$  for all energy levels since the wave function is dominated by the exponential term and nonzero  $\gamma$  makes only a small quantitative difference. In the transition metal series, the atomic term values are near 1 Ry and the approximation is an excellent one. Normalizing the wave functions to 1 gives a radial wave function

$$R_l(r) = 2 \mu^{3/2} e^{-\mu r} \quad . \quad (II.8)$$

This form of the wave function may be combined with Eqs. (II.1) and (II.3) to give the band width as

$$W_{l\infty} = \frac{16 (-\epsilon)(\mu r_0) e^{-2\mu r_0}}{1 - 2\mu^2 r_0^2 e^{-2\mu r_0}} \quad , \quad (II.9)$$

and the center of gravity of the band as

$$C_{l\infty} = \epsilon_l + \frac{\Omega_0}{\Omega} W_{l\infty} \mu^3 / \pi e^{-2\mu r_0} \quad . \quad (II.10)$$

The  $\infty$  symbol is used to designate the large- $r$ , asymptotic analytic form of the wave function. The band width and center of gravity are still dependent upon the angular momentum quantum number  $l$  thru the value of the atomic term value  $\epsilon_l$ . The approximation works best with  $l = 0, 1, 2$  (s,p,d-states) but gives quite reasonable results for  $l=3$  (f-states) as well.

### III. ATOMIC CORE LEVELS UNDER COMPRESSION

#### A. Core States From A Band-Structure Picture

In a metal at zero pressure, we can divide the electrons into two groups, the conduction electrons and the core electrons. The conduction electrons are primarily responsible for the cohesive energy in a metal. The core electrons are considered to be those whose orbitals are initially unchanged from the orbitals in an isolated atom and are much more tightly bound to the nucleus. We now wish to consider the situation whereby the core electrons begin to "see" one another when the overlap of their wave functions becomes finite as the compression increases. One should picture

the process as the evolution of zero width atomic states on individual sites changing into narrow width band states that extend over the entire system.

Strictly speaking, whenever core electrons interact with one another they also interact with all the conduction electrons plus all of the other core electrons. A quite reasonable approach is to first treat the interaction for a given angular momentum core state between ions on adjacent sites and then add the hybridization between different core angular momentum states. This is similar to the procedure of band theory. For instance, the s-s, p-p, d-d, etc. interactions are treated separately and only when there is actual overlap of the resulting bands will s-p, s-d, etc. hybridization be important since that interaction goes as the inverse of the energy difference between states. The evolution of core states from zero width atomic levels into broadened bands is a continuous process and one would expect that LCAO's would be an appropriate expansion set. Also, the ASM is well suited to this problem because the approximations involved are such that it limits exactly to Hartree-Fock atoms at infinite separation.

The results for nickel using the ASM and Hartree-Fock tables in the formulae in Section II are shown in Fig. 1 for the band widths and Fig. 2 for the relative positions of the bands. Both sets of curves are plotted as a function of  $r_0$ . The ASM results are in excellent agreement with full band calculations. For a value of  $r_0$  just greater than  $1 a_0$  ( $a_0$  = Bohr radius), the band widths for the 3s, 3p, and 3d orbitals equal one another and are also equal to the band width of free electrons. The 3s, 3p, and 3d bands also overlap one another near  $r_0 = 1.3 a_0$ . The zero pressure density corresponds to a value of  $r_0 = 2.61 a_0$ .

Missing from Fig. 2 is the s-p conduction band that is strongly coupled to the 3d band thru hybridization. The ASM can be used to provide all the parameters for the entire band structure in the solid using the method of Harrison and Froyen.<sup>7</sup> The results for Ni at normal density are given in Ref. 1. To do the full band calculation, one must determine the average d-band energy and the hybridization matrix elements between the d-orbitals and the s-p conduction band. The average d-band energy may be determined entirely from neutral-atom atomic term values (and  $r_0$ ). The procedure involves using the renormalized atom approach of Watson, Ehrenreich, and Hodges<sup>8</sup>, the energy of the bottom of the conduction band as given by Froyen<sup>6</sup>, and the coulomb energy required to shift an atomic electron from a

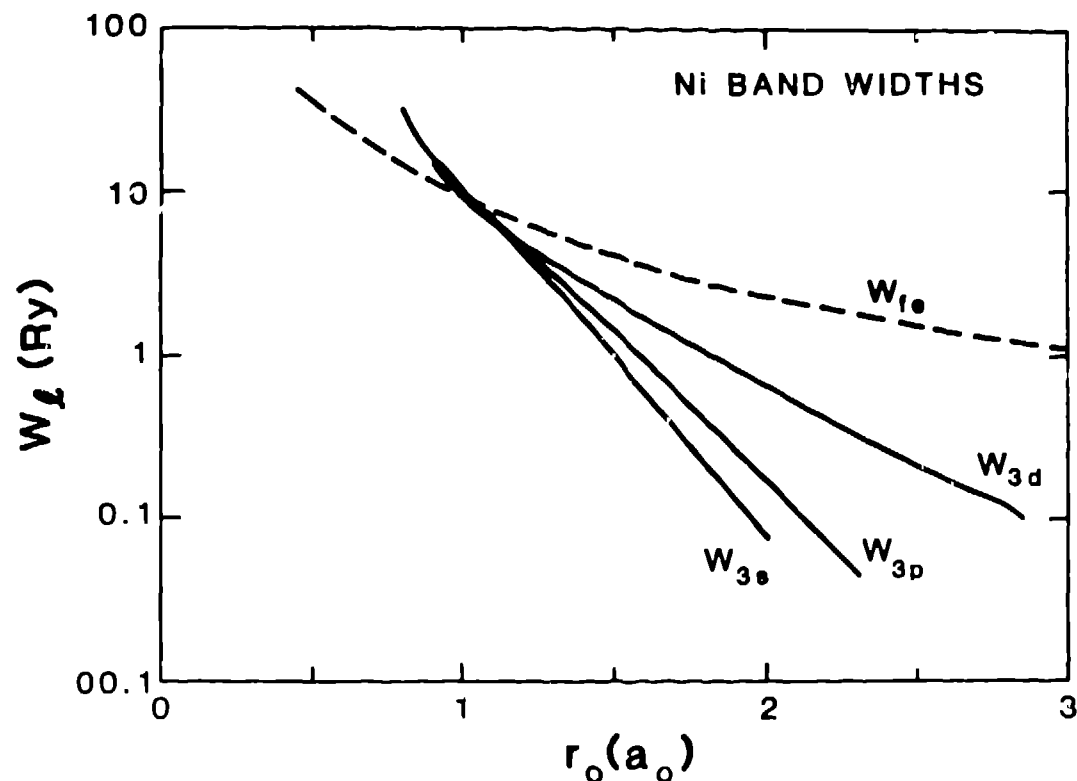


Fig. 1. The widths for the 3s, 3p, and 3d bands of nickel as a function of  $r_0$ . The dashed line is the band width for a system of free electrons. All of the band widths including the free electron width become equal at the same value of  $r_0$ .

s-orbital to a d-orbital. (See Eq.(27) of Ref. 1) The hybridization matrix element can be evaluated using the asymptotic form of the radial wave function with all of the resulting parameters again determined from atomic term values.

#### B. Analytic Treatment of the Relative Movement of Different Angular Momentum Bands

The formulas of Sec. II can be used to determine the analytic dependence of the relative movement under compression for bands with different orbital angular momentum quantum numbers. This may be accomplished in two ways, first, by using the asymptotic form of the radial wave function given in Eq. (II.5), and second, by using Andersen's muffin-tin-orbital theory<sup>7</sup> to obtain the functional dependence of the wave function upon  $r_0$ .

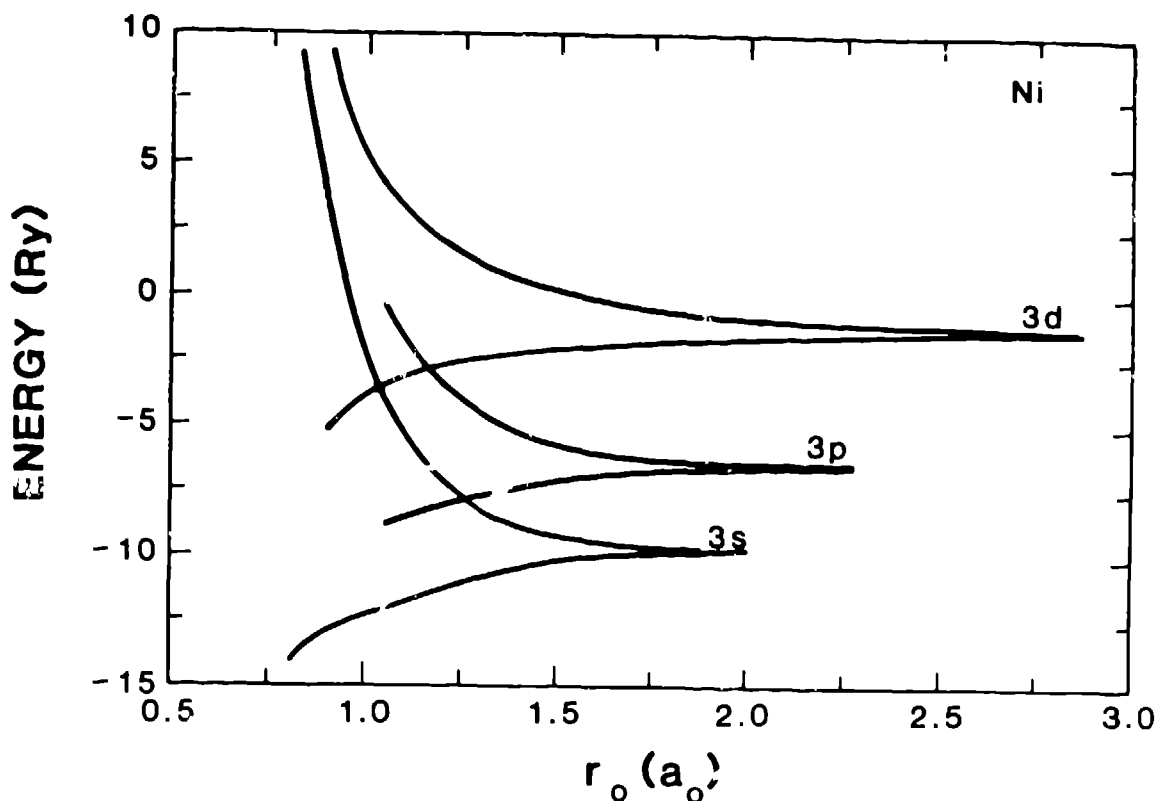


Fig. 2. The bottom, center, and top of the 3s, 3p, and 3d bands of nickel. The 3d band was calculated in the same manner as the 3s and 3p bands and does not include any hybridization with the conduction band.

The overlap integral may also be obtained from Eq. (II.3), (II.5), and the electron density  $\rho = R_{\lambda}^2/4\pi$ . The result is

$$S_{\lambda} = 8/3 \mu_{\lambda}^3 r_0^3 e^{-2\mu_{\lambda}r_0} \quad (III.1)$$

The exponential term dominates the  $r_0$  dependence in all cases with  $W_{\lambda}$  and  $S_{\lambda}$  varying as  $\exp(-2\mu_{\lambda}r_0)$  and  $C_{\lambda}$  varying as  $\exp(-4\mu_{\lambda}r_0)$ . Values for a sampling of elements are given in Table I. For all elements,  $\mu_s > \mu_p > \mu_d$  for the same value of  $n$ , the principal quantum number. Thus, the s-band will rise in energy with respect to the p-band as  $r_0$  decreases, the p-band will rise with respect to the d-band, and so forth. This result is easily seen in Fig. 1 for the band widths as well as the domination of the exponential term. In the f-shell elements the situation is more complicated. For instance, in tungsten  $\mu_{4f}$  lies between  $\mu_{5s}$  and  $\mu_{5p}$ , but



TABLE I.

Values of  $\mu_l$  for selected core states. The values of  $r_0$ , in units of Bohr radii  $a_0$ , are for zero pressure. The  $\mu_l$  are calculated from the tables of Mann<sup>5</sup> and are in units of  $1/a_0$ . The number preceding the angular momentum label is the principal quantum number.

	$r_0$	2s	2p		
Na	3.94	2.37	1.74		
Al	2.98	3.13	2.54		
		3s	3p	3d	
Mn	2.70	2.78	2.24	1.06	
Fe	2.67	2.89	2.35	1.10	
Ni	2.61	3.13	2.56	1.18	
		4f	5s	5p	5d
Eu	2.27	1.10	1.91	1.47	
W	2.95	2.10	2.42	1.93	0.90
		5f	6s	6p	6d
U	3.21	1.13	1.83	1.44	0.73

the predictions for the density dependence of the bands should still be reliable for small band widths. Improved numerical results are possible using atomic wave functions that include relativistic corrections.

Muffin-tin-orbital theory gives a similar prediction for the relative motion of the bands. In muffin-tin-orbital theory we note that the local orbitals vary as  $r^{-l-1}$  at and beyond the atomic sphere if the muffin-tin zero is taken at the free-atom energy. Thus, the electron density varies as  $r^{-2l-2}$  and the band width is

$$W_l = \hbar^2 / m 4\pi (2l+2) r_0 \rho_l \sim 1/r_0^{2l-1} \quad . \quad (\text{III.2})$$

The overlap integral and center of gravity of the band are dependent upon  $r_0$  by

$$S_l \sim 1/r_0^{2l-1} \quad , \quad C_l \sim 1/r_0^{4l} \quad . \quad (\text{III.3})$$

One obtains the same result as with the asymptotic form of the wave function, namely, a band with a smaller value of  $l$  will rise faster in energy relative to a band with a larger value.

### C. Transition to Free-Electron Bands

At extremely large compressions, the bands will completely overlap as shown in Fig. 2 and may be considered free-electron bands. For  $s$  and  $p$  bands the free-electron band width can be written (bcc structure)

$$W_{fe} = 2\pi^2 (3/8\pi)^{1/3} 2\hbar^2/m r_0^2 \quad . \quad (III.4)$$

In Fig. 1, the  $s$ ,  $p$ ,  $d$  widths become equal and also equal to the free-electron width near the same value of  $r_0$ , and all may be treated as free-electron bands.<sup>1</sup> Another aspect of the identification with free-electron bands is their energy ordering, which should be  $s, p, d$ . In sodium and aluminum this same energy ordering also occurs as the  $3s$  band moves above the  $3d$  band (and above the Fermi energy) and the bands become ordered  $2s, 2p, 3d$ . It should be noted that free-electron behavior occurs at extremely large compressions (a factor of 50 to 100) and corresponds to pressures of over 1000 Mbars. Perhaps more important is the result that an entire shell of electrons with the same principal quantum number  $n$  becomes free-electron-like at the same compression rather than one  $l$ -orbital at a time. For instance, in sodium and aluminum all 8 electrons in the  $n=2$  shell become free-electron-like instead of first the 6  $p$ -electrons and later the 2  $s$ -electrons. The  $n=2$  electrons are then describable by simple metal theory, but with an ionic charge of  $Z=11$  for aluminum and  $Z=9$  for sodium. Similarly for nickel, the 16  $n=3$  electrons become free-electron-like together.

### IV. SUMMARY

The electronic structure for core states of nickel has been calculated using the Atomic-Surface-Method. The evolution of the core electrons from isolated free-atom states to narrow bands and finally to free-electron behavior has been described in a simple theory that allows the determination of the analytic dependence of the electronic structure upon density. One finds that the band widths of an entire shell of electrons

with the same principal quantum number become free-electron-like at the same density. In the case of nickel, this means that all 16 of the  $n=3$  shell of electrons approach free electron behavior together.

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