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Analysis of the electronic pressure in transition and noble metals

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Particularly with transition and noble metals in mind, we analyze the pressure in a solid in terms of the (bulk) wave functions evaluated at the surface of the atomic (Wigner-Seitz) sphere. The partial pressures (angular-momentum decomposed) are further split into a number of terms to which some physical significance can be attributed. Calculations within the local-density scheme are presented for copper, silver, and gold over a large range of volumes. It is argued that one term represents a strong pairwise repulsion between full *d* shells, balanced (at equilibrium) by a strong inward pressure due to the *sp* electrons. The latter is interpreted as a volume force driven by the atomic pseudopotential including the *sp* hybridization with the *d* states. The application of this picture to the understanding of surface instabilities in these metals is mentioned, but details of such investigations are given elsewhere. Also the observation that Cu, Ag, and Au in compounds where the *d* shells are kept out of contact tend to have substantially smaller volumes is understood from the present analysis.

I. INTRODUCTION AND SUMMARY

A physical understanding of the trends of the observed cohesive and elastic properties through the transition-metal series can be obtained from the effects of the gradual filling of the electronic *d* states. This was, for example, clearly demonstrated by the analysis of band-structure calculations by Pettifor[1] and by Moruzzi *et al.*[2] As an example of such trends, let us consider the bulk moduli B of the $3d$, $4d$, and $5d$ series as presented in Fig. 1. Going from the low-Z end towards the middle of a series, the lowest lying, bonding *d* states are gradually being filled, providing a numerically increasing negative partial pressure, i.e., leading to a contraction of the crystal. This simultaneously causes *s* and *p* electrons to be expelled into the outer parts of the Wigner-Seitz cell which hardens the solid, i.e., leads to an increase in B. Proceeding from the middle of a series towards the upper end, the noble metals, the *d* bands, become filled,[3] i.e., also the antibonding states are occupied. Consequently, the *d* pressures decrease again in magnitude, the lattice relaxes, and the interstitial electron density is simultaneously reduced. This explains the drop in magnitude of the bulk moduli in the high-Z end of the transition series (Fig. 1).[4]

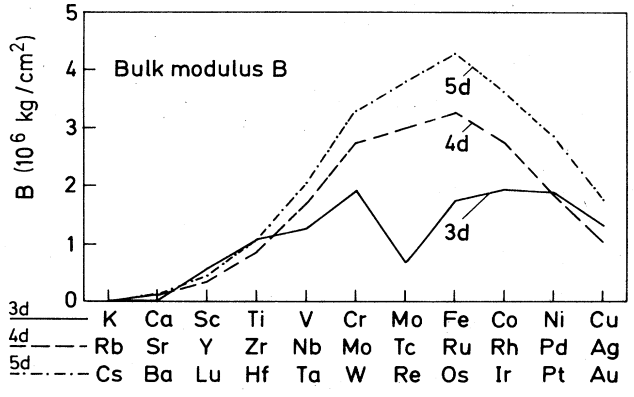

FIG. 1. Bulk modulus B (observed) of transition metals.

The classical works[5,6] by Fuchs were probably the first to stress the importance of understanding the closed-shell interactions in order to be able to arrive at a physical picture of the cohesive properties of the noble metals. He[5,6] viewed the forces between the closed shells as composed of an "attractive van der Waals force and a repulsive force due to the overlapping of the closed shells." The latter he treated as additive central forces. Later, total-energy calculations, using[7,8] expressions which to some extent are parametrized, were able to reproduce well the experimental results. Physical models based on detailed band-structure models[9–12] have appeared since the pioneering work by Deegan.[9] The parametric approaches have sometimes assumed that the interaction between the *d* electrons in the noble metals could be described as a Born-Mayer type of repulsive term, ignoring the substantial[13] van der Waals attraction and the attractive effect of *sp*-*d* hybridization. Note that at the interatomic distances considered here, the "van der Waals" interaction is no longer simply that due to induced dipole fluctuations but more generally due to electron correlation around the atomic overlap and is indeed quite well given[14] by self-consistent band-structure calculations in conjunction with the local-density approximation[15–17] (LDA). Thus Kollar and Solt[12] concluded for copper that the *d* shells give a small net attraction at equilibrium, in agreement with Fuchs,[5,6] rapidly becoming repulsive at a smaller lattice constant. We agree with this picture but only if the *d* pressure is taken to include the effect of *sp*-*d* hybridization on the *d* shells.

The perspective of the present work is somewhat different. It is to analyze the interaction in the noble metals as a balance between pairwise and volume forces in order to understand the structural rearrangements[18,19] found at the surfaces of the noble metals, particularly gold, where this balancing is destroyed.[20,21] By a "volume" force in this context we have in mind the effect of the *sp*-electron density (which is determined by an environment of several atoms) interacting with the one-atom pseudopotential. We shall argue[20] that the total effect of *sp*-*d* hybridization is to a very good approximation a one-atom "volume" force in the above sense and hence is to be included for our purposes with the volume force of the *sp* electrons. We then find that the total *volume* force is strongly *attractive,* balanced in the bulk noble metals by a strong net *pairwise repulsion* from the full *d* shells.

A more direct application of this model can be made in an analysis of the data on metal—noble-metal (MN) alloys as noted by Nevitt.[22] He pointed out that in compounds where the *d* shells are kept out of "contact," Cu, Ag, and Au tend to have a smaller atomic volume. He analyzed the volumes of MN alloys with the CsCl structure and found that the molecular volumes Ω can be fitted quite well by

$$\Omega=\Omega_N^*+\Omega_M \ , \tag{1}$$

where Ω_M is the atomic volume of the pure metal M and Ω_N^* is an *apparent* volume of the noble-metal N atom in the alloy. This, Ω_N^*, turns out[22,23] to be approximately the same for a given noble metal in many alloys and *smaller* than the atomic volume Ω_N of the noble metal. It was found[20] that $\Omega_N-\Omega_N^*$ is about 1.8, 1.2, and 3 Å^3 for Cu, Ag, and Au, respectively. The part of the *d* partial pressure which we identify as the *d*-shell pairwise interaction will later be referred to as $P_{c1}(d)$. By calculating, as a function of volume, the difference $P_{\text{tot}}-P_{c1}(d)$, we are able to estimate $\Omega_N-\Omega_N^*$, and we shall see that our results agree with Nevitt's conclusion.

Clearly, in order to understand volume and pairwise forces from the band structure due to the different electrons, it is necessary first to decompose the total pressure P into different l components P_l, and then analyze these further into separate physical effects. The paper is therefore organized as follows. In Sec. II we discuss the slightly thorny subject of the formulas for total pressure (Sec. II A) and partial pressures P_l (Sec. II B), including the sense in which such a decomposition is physically meaningful. Quantitative results for the various components are given in Sec. III, while Sec. IV discusses the results, including the volume (one-atom) nature of the hybridization. Section IV also contains a calculation of the "noble-metal contraction" in the MN alloys in the sense discussed above in connection with Eq. (1). Here good agreement with experiment[20,22,23] adds conclusiveness to the work.

II. PARTIAL PRESSURES

The formulas for electronic pressures in solids by Niemenen and Hodges[24] and Pettifor[25] are well known and widely used in connection with local-density calculations. They are often applied in theoretical predictions of equilibrium volumes, and further, via orbital decompositions into "partial pressures," they offer possibilities of gaining some insight into bonding characteristics. Also known is the derivation of these equations by the elegant method based on Andersen's "force theorem."[26–28]

Nevertheless, we find it appropriate here to review their derivation briefly (Sec. II A). This serves to define the parameters that enter our calculations, and to state clearly what we mean here by an "l partial pressure," distinguishing it from what we consider as an unphysical decomposition based on a meaningless separation of the total energy into "l components." Then in Sec. II B we present approximate pressure relations which can be broken up into terms to which we can attribute physical significance. Again the formulas are not claimed to be new, but the literature is rather confusing due to various identities and alternatives, so that it would be cumbersome for the reader to fit the jigsaw puzzle together from the original sources.[26–29] Furthermore, our discussion of the relations between the different formulations and of the physical significance of the terms is much more complete than previously, as is essential for our ultimate goal of identifying and calculating the volume and pairwise interactions.

A. Definitions

We consider the simplest possible solid, a crystal with only one kind of atom per lattice site, i.e., an elemental solid. This means that we avoid complications to our definitions of partial pressures arising from Madelung contributions. Further, we assume that we can apply the atomic-sphere approximation[29] (ASA), i.e., the Wigner-Seitz cells are replaced by (neutral) spheres inside which the electron density and the potential are made spherically symmetric. In this case the force theorem (FT)[26–28] states that a distortion of the system (expansion or other change of atomic positions) causes a change in the total energy which to first order (see also Refs. 30—32) can be calculated as

$$\delta U=\delta \int EN(E)dE \ , \tag{2}$$

where $N(E)$ is the density-of-states function obtained from the one-particle energy spectrum. The right-hand side, the change in one-particle energy sum, is assumed to be evaluated by the so-called "frozen-potential" approach.[26,30–32] If we had not assumed the ASA, Eq. (2) would have an extra term, a change in electrostatic interaction between the "cells" which are cut loose and moved to their new positions during the virtual displacement as described in connection with the derivation of the FT.[26]

The change in total energy following an expansion, where the Wigner-Seitz radius is changed from S to $S+\delta S$, is (per atom)

$$\delta U=-4\pi PS^2\,\delta S=-3P\Omega\,\delta\ln S \ , \tag{3}$$

where P is the pressure and Ω the cell volume. This gives, with (2),

$$3P\Omega=-\frac{\delta}{\delta \ln S}\int_{-\infty}^{E_F} EN(E)dE \ . \tag{4}$$

In terms of the number of states, $n(E)$ [integral of $N(E)$], this is

$$
\begin{aligned}
3P\Omega &= -\frac{\delta}{\delta \ln S}\left[E_F n(E_F) - \int_{-\infty}^{E_F} n(E)dE\right] \\
&= -\left[\frac{\delta E_F}{\delta \ln S} n(E_F) + E_F \frac{\delta n(E_F)}{\delta \ln S} - \frac{\delta E_F}{\delta \ln S} n(E_F) \right. \\
&\qquad \left. - \int_{-\infty}^{E_F} \frac{\delta n(E)}{\delta \ln S} dE\right] \\
&= \int_{-\infty}^{E_F} \frac{\delta N(E)}{\delta \ln S} dE \; .
\end{aligned}
\tag{5}
$$

We have used the fact that $\delta n(E_F)=0$, following the definition of the Fermi level. Now, let $\underline{D}$ denote the logarithmic derivatives[29] $\{D_l(E)\}$ (l is the angular momentum). The total number of states n is a canonical function of $\underline{D}$ in the sense that the functional dependence of n on D_0, $D_1, \ldots$, is given entirely by the structure constants in the canonical band theory.[29] This means we can write the nontrivial formula for the partial density of states $N_l(E)$

$$
N_l(E) \equiv \frac{dn_l(E)}{dE} = \frac{\partial N(\underline{D})}{\partial D_l} \dot{D}_l \; , \tag{6a}
$$

where $\dot{D}_l$ is the energy derivative of D_l. Note how this formula differs from the more obvious (and also correct) result of total differentiation

$$
\frac{dn_L}{dE} = \sum_{l'} \frac{\partial n_l}{\partial D_{l'}} \frac{dD_{l'}}{dE} \; , \tag{6b}
$$

which mixes l and l'. We can transform (6a) further into

$$
N_l(E) = \frac{\partial n(\underline{D})}{\partial D_L} \dot{D}_l = \left[\frac{\partial n}{\partial D_l}\right] \left[-\frac{1}{S\phi_l^2(E,S)}\right] \; , \tag{7}
$$

where we have used the relation given in Ref. 29 to express $\dot{D}_l$ in terms of the radial partial wave amplitude, $\phi_l(E,S)$ at the sphere surface, $r=S$. Thus we have

$$
\begin{aligned}
3P\Omega &= \int_{-\infty}^{E_F} \frac{\delta n(E)}{\delta \ln S} dE \\
&= \sum_l \int_{-\infty}^{E_F} N_l(E) S \phi_l^2(E,S) \left[-\frac{\delta D_l(E)}{\delta \ln S}\right] dE
\end{aligned}
\tag{8a}
$$

or

$$
3P\Omega = \sum_l 3P_l \Omega \; , \tag{8b}
$$

where the *l partial pressure* P_l is defined through

$$
3P_l \Omega = \int_{-\infty}^{E_F} N_l(E) S \phi_l^2(E,S) \left[-\frac{\delta D_l(E)}{\delta \ln S}\right] dE \; . \tag{9}
$$

Using the (radial) Schrödinger equation one easily shows that

$$
\begin{aligned}
-\frac{\delta D_l}{\delta \ln S} &= \{[D_l(E)+l+1][D_l(E)-l] \\
&\qquad + S^2[E - \varepsilon_{\mathrm{xc}}(S) + \mu_{\mathrm{xc}}(S) - V(S)]\} \; ,
\end{aligned}
\tag{10}
$$

where $V(S)$ is the ASA potential at $r=S$. Also, $\mu_{\mathrm{xc}}(S)=\mu_{\mathrm{xc}}(\rho(S))$ is the exchange-correlation potential (LDA) evaluated for the electron density of the sphere surface and $\varepsilon_{\mathrm{xc}}(S)$ is the LDA exchange-correlation energy at $r=S$. Equations (8)—(10) specify how we have calculated the partial pressure when we refer to it in the following sections.

We shall now, on the other hand, specify what we do *not* consider as a proper definition of partial pressures. Of course $N(E)=\sum_l N_l(E)$ and thus

$$
\sum_l 3P_l \Omega = -\frac{\delta}{\delta \ln S} \sum_l \int_{-\infty}^{E_F} E N_l(E) dE \; . \tag{11}
$$

However, a quantity P_l^* defined through

$$
3P_l^* \Omega = -\frac{\delta}{\delta \ln S} \int_{-\infty}^{E_F} E N_l(E) dE \tag{12}
$$

$$
\begin{aligned}
&= \frac{\delta}{\delta \ln S}\left[E_F n_l(E_F) - \int_{-\infty}^{E_F} n_l(E) dE\right] \\
&= \left[E_F \frac{\delta n_l(E_F)}{\delta \ln S} - \int_{-\infty}^{E_F} \frac{\delta n_l}{\delta \ln S} dE\right]
\end{aligned}
\tag{13}
$$

is *not* identical to P_l given in (9), as can be shown numerically or analytically. Thus we have $P_l^* \neq P_l$, but of course the "sum rules"

$$
\sum_l P_l^* \Omega = \sum_l P_l \Omega, \quad \sum_l \delta n_l(E_F) = 0 \tag{14}
$$

apply. Incidentally, we wish to point out that the relation

$$
3(P_l^* - P_l)V = -E_F \frac{\delta n_l(E_F)}{\delta \ln S} \; , \tag{15}
$$

which might appear plausible from (8a) and (13) also *does not* hold: it corresponds to forgetting the $l' \neq l$ terms in (6b). If we had considered P_l^* as the partial pressure, Eq. (12) would have been rewritten as

$$
\delta U = \sum_l -P_l^* \delta\Omega = \delta \int E \sum_l N_l(E) dE \equiv \sum_l \delta U_l \; , \tag{16}
$$

from which one might be tempted to identify "angular-momentum components of the total energy" as $U_l = \int E N_l(E) dE$. The introduction of such a quantity does not make any sense due to electron-electron interactions, and even if it did make sense the definition (16) from P_l^* would be incorrect because it neglects the l,l' mixing in (6b).

To what extent can the l decomposition of the total pressure be physically significant? The interaction energy between energy carriers or modes is by definition due to their mutuality and not ascribable to one or another. The same must in some sense be true of the pressure viewed as the volume derivative of the energy. Certainly the radial wave function for one l contributes to the self-consistent potential in the Schrödinger equation for another l' and hence to $P_{l'}$. But in the case of pressure one has the alternative kinetic viewpoint[33] in which the pressure is physically due to particles hitting the boundary, their momentum being influenced by and, hence, containing implicit information about the potential forces acting on them.

The pressure in this formulation contains three terms in general, the first being the one-particle kinetic pressure which can be decomposed with respect to l, and the second an electrostatic long-range term which is zero for neutral atomic spheres. The third term corresponding to the last part of (10) comes from exchange and correlation which are Coulomb interaction effects, but even here we see from (9) that the term is proportional to the density

$$\int N_l(E)\phi_l^2(E,S)dE$$

of l electrons at the sphere radius, so that we picture the exchange and correlation hole as "dressing" the electron into a quasiparticle (which in LDA has zero spatial extent) and the third pressure term as dressing the first term to turn it into the momentum pressure due to quasiparticles. The *sp-d* hybridization does not affect the l decomposition as discussed below.

To make the legitimacy of a pressure decomposition even clearer, we refer to a perfect gas of molecules which have internal rotational and vibrational degrees of freedom. The pressure is due purely to the kinetic momentum, but as we compress the gas adiabatically, part of the work pumped directly into the kinetic energy is transferred continuously into rotational and vibrational energy. Thus it would be quite incorrect to integrate the kinetic pressure and call that the kinetic energy.

B. Approximate pressure equations

This section gives two sets of simplified pressure relations which do not possess the same accuracy as Eqs. (8)–(10) but are useful for interpretating the calculated quantities in the case of tight-binding and nearly-free-electron bands, respectively. We shall also define here what later will be referred to as "central pressures" and "tail pressures."[34]

It was mentioned in Sec. II A that the number of states $n=n(\underline{D})$ is a canonical function of $\underline{D}=\{D_l\}$. We can, of course, equally well consider it as a canonical functional $n=n(\underline{\mathscr{P}})$, $\underline{\mathscr{P}}=\{\mathscr{P}_l\}$ of the potential functions[29,35]

$$\mathscr{P}_l(E)=2(2l+1)\frac{D_l(E)+l+1}{D_l(E)-l} \tag{17}$$

to derive alternative pressure formulas. For the energy derivative of D_l we had

$$\dot{D}_l(E)=\frac{-1}{S\phi_l^2(E,S)} \, . \tag{18}$$

A similar relation for $\mathscr{P}_l$ is[26,28]

$$\dot{\mathscr{P}}_l(E)=\frac{1}{\frac{1}{2}S\chi_l^2(E,S)} \, , \tag{19}$$

where $\chi_l(E,r)$ is the radial part of the muffin-tin orbital.[29] The band center, C_l is the energy[29,35] where $\mathscr{P}_l(E)$ is zero, i.e., where from Eq. (17), $D_l(E)=D_l(C_l)=-l-1$. For energies in the neighborhood of C_l, we may use the first-order expansion

$$\begin{aligned}\mathscr{P}_l(E)&\simeq(E-C_l)\dot{\mathscr{P}}_l(C_l)\\ &=(E-C_l)\frac{1}{\frac{1}{2}S\chi_l^2(C_l,S)}\\ &=(E-C_l)\frac{1}{\frac{1}{2}S\phi_l^2(C_l,S)}\\ &=(E-C_l)(S^2\mu_l) \, ,\end{aligned} \tag{20}$$

where μ_l is the (central) l-band mass parameter.[29] The bandwidth parameter W_l is inversely proportional to μ_l (see Ref. 29):

$$W_l \propto \frac{1}{\mu_l S^2} \, . \tag{21}$$

The approximation (20) suffices in the neighborhood of a tight-binding (TB) band, i.e., for the d pressures in the noble metals in the present work and for the $5p$ states in compressed Xe.[14] However, approximation (20) is not adequate for nearly-free-electron (NFE) bands and for the high-l tails from orbitals on neighboring atoms, in both cases the radial wave function for pseudowave function being nearly the spherical Bessel function. We then expand around the energy corresponding to the[29] "square-well pseudopotential," V_l:

$$\mathscr{P}_l(E)\simeq(E-V_l)\dot{\mathscr{P}}_l(V_l) \, . \tag{22}$$

Again we use (19), but with[28]

$$\tfrac{1}{2}S\chi_l^2(E,S)=\frac{\tau_l S^2(E-V_l)^2}{2(2l+1)^2(2l+3)} \, , \tag{23}$$

i.e.,

$$\mathscr{P}_l(E)\simeq\frac{2(2l+1)^2(2l+3)}{S^2\tau_l}\,\frac{1}{E-V_l} \, , \tag{24}$$

where τ_l is the "band-bottom mass parameter."[28] It follows that the change in the single-particle energy sum [Eq. (2)] which enters in the pressure equation [Eq. (4)] can, approximately, be written[26] as

$$\begin{aligned}\delta\int_{-\infty}^{E_F}EN(E)dE=-\int_{-\infty}^{E_F}\delta n(E)dE=-\sum_l\frac{\partial n}{\partial\mathscr{P}_l}\delta\mathscr{P}_l dE=&\underset{\text{(central)}}{\sum_{l\in\underline{l}_c}} n_l(E_F)[\delta C_l+(\langle E\rangle_l-C_l)\delta\ln W_l]\\ &+\underset{\text{(tail)}}{\sum_{l\in\underline{l}_t}} n_l(E_F)[\delta V_l-(\langle E\rangle_l-V_l)\delta\ln(\tau_l S^2)] \, .\end{aligned} \tag{25}$$

Here, $\langle E\rangle_l$ means the center of gravity of the occupied part of the l band. In the first sum, l takes only the values $l\ (\in \underline{l}_c)$ for TB bands where we can use the *central* expansion [Eq. (20)]; in the second sum only those values l $(\in \underline{l}_t)$ for the NFE bands and high-l tails where the "*tail*" expansion [Eq. (24)] is used. Thus, for a noble metal,[36] we would have $\underline{l}_c=\{2\}$, $\underline{l}_t=\{0,1,3,\dots\}$.

The approximate pressure relations thus lead to a decomposition into "central pressures" P_c and "tail pressures" P_t:

$$P=\sum_{l\in \underline{l}_c} P_c(l)+\sum_{l\in \underline{l}_t} P_t(l)\ , \tag{26}$$

where

$$3P_c(l)\Omega\cong -n_l\left[\frac{\delta C_l}{\delta \ln S}+(\langle E\rangle_l-C_l)\frac{\delta \ln W_l}{\delta \ln S}\right] \tag{27}$$

and

$$3P_t(l)\Omega\simeq -n_l\left[\frac{\delta V_l}{\delta \ln S}-(\langle E\rangle_l-V_l)\frac{\delta \ln(\tau_l S^2)}{\delta \ln S}\right]\ . \tag{28}$$

Note that here and elsewhere the differentiation with respect to $\ln S$ has to be carried out according to the prescription of the force theorem.[26] Each of the relations (27) and (28) can be broken into three terms giving three central pressures P_{c1}, P_{c2}, and P_{c3} and three tail pressures P_{t1}, P_{t2}, and P_{t3}. This division is made by applying the relations (perturbation theory) given as (79) in Ref. 26. The three central pressures are

$$\begin{aligned}3P_{c1}(l)\Omega&=-n_l\frac{\delta C_l}{\delta \ln S}\\ &=\frac{2n_l}{\mu_l}[C_l-V(S)+\mu_{\mathrm{xc}}(S)-\varepsilon_{\mathrm{xc}}(S)]\ ,\end{aligned} \tag{29a}$$

$$3P_{c2}(l)\Omega=n_l[\langle E\rangle_l-C_l]\left[2l+1+\frac{2}{\mu_l}\right]\ , \tag{29b}$$

$$\begin{aligned}3P_{c3}(l)\Omega=&-n_l(\langle E\rangle_l-C_l)\frac{2S^2}{D_{\dot{\nu}}+l+1}\\ &\times\{[C_l-V(S)+\mu_{\mathrm{xc}}(S)-\varepsilon_{\mathrm{xc}}(S)]\}\ .\end{aligned} \tag{29c}$$

The tail pressures P_{t1}, P_{t2}, and P_{t3} are given by

$$\begin{aligned}3P_{t1}(l)\Omega&=-n_l\frac{\delta V_l}{\delta \ln S}\\ &=n_l\frac{2l+3}{\tau_l}[V_l-V(S)+\mu_{\mathrm{xc}}(S)-\varepsilon_{\mathrm{xc}}(S)]\ ,\end{aligned} \tag{30a}$$

$$3P_{t2}(l)\Omega=n_l(\langle E\rangle_l-V_l)\left[-(2l+1)+\frac{2l+3}{\tau_l}\right]\ , \tag{30b}$$

$$\begin{aligned}3P_{t3}(l)\Omega=&-n_l(\langle E\rangle_l-V_l)\\ &\times\left[\frac{2S^2}{D_{\dot{\nu}}-l}[V_l-V(S)+\mu_{\mathrm{xc}}(S)-\varepsilon_{\mathrm{xc}}(S)]\right]\ .\end{aligned} \tag{30c}$$

Here, $D_{\dot{\nu}}$ is the logarithmic derivative of the energy derivative of the partial wave $\dot{\phi}_{\nu l}$ (see Ref. 29).

We turn now to the physical significance and signs of the terms in (29). The partial pressure contribution P_{c1}, Eq. (29a), is clearly related to the shift in energy position of the l band as a whole when the crystal volume is changed, i.e., the "center-motion term." At short distances it is positive due to the exclusion principle as the neighboring shells overlap, while at larger distances it is negative due to the van der Waals interaction in the sense discussed in Sec. I. The other two central pressures (29b) and (29c) may be named band-filling terms since they both are proportional to $\langle E\rangle_l-C_l$, i.e., the difference between the actual center of gravity $\langle E\rangle_l$ of the band (the occupied part) and the canonical center C_l. The P_{c2} and P_{c3} necessarily have opposite signs since the postfactors in large parentheses in (29b) and in curly brackets in (29c) are positive (as is $D_{\dot{\nu}}$). The P_{c3} is an exchange and correlation dressing in the sense discussed and is usually considerably smaller than P_{c2}. For an isolated canonical band, C_l is the center of the band so that for a filled ideal band we would have $\langle E\rangle_l-C_l=0$. For a partially filled TB band $\langle E\rangle_l-C_l$ is negative corresponding to the filling of the bonding states more than the antibonding ones, giving a strong negative $P_{c2}+P_{c3}$. Two further effects in $\langle E\rangle_l-C_l$ and hence in $P_{c2}+P_{c3}$ may be seen which can become important, particularly in the case of full TB bands, as[3] for the noble-metal d shells. Firstly,[37] bonding in a TB interpretation implies that the tails of the atomic orbitals overlap the atomic spheres of neighboring atoms, and in our formalism get expanded about the centers of those *other* atoms to yield small partial densities of states of all angular momenta. Thus there is a small loss of weight from the full[3] l band into all other l' which we call the *bonding redistribution.* Bonding states at the bottom of the band have a longer range (larger amplitude for $r=S$) than the antibonding states at the top where an ideal antibonding state has a node at $r=S$. We therefore expect[37] $\langle E\rangle_l-C_l>0$ from this effect, yielding a positive $P_{c2}+P_{c3}$. The second effect is that of *hybridization.* The mixing of the l-band orbitals with other TB or NFE bands results in a nonzero (essentially positive) l partial density of states $N_l(E)$ for all E where there are occupied states below the Fermi level. Conversely, $N_{l'}(E)$ for $l'\neq l$ will be nonzero in the energy range of the TB l band. In addition, the energies of the bands will be shifted. Consequently, $\langle E\rangle_l-C_l$ may have either sign from hybridization, and since energy level from l and l' bands mutually repel, we may expect a large measure of cancellation between the l and l' partial pressures for ll' hybridization. In the extreme limit of two filled ideal TB bands, their $P_{c2}+P_{c3}$ contributions must cancel exactly.

A similar analysis[26] can be made for the tail partial pressures (30). Here, V_l represents the mean pseudopotential felt by the electrons, i.e., the bottom of the band for the relevant l, and thus P_{t1} contains the movement of the band as a rigid whole with variation in atomic-sphere radius as seen from the first form in (30a). It also contains the exchange and correlation energy as is evident from the second form in (30a) which arises, as already remarked, by differentiating V_l in the manner of the force theorem.[26]

The $P_{t2}+P_{t3}$ together give for a free-electron gas the kinetic Fermi pressure as is most easily seen from the second term of (28), and indeed $P_{t2}+P_{t3}$ are probably always best considered combined.

We now give an order-of-magnitude discussion of the pressures for the noble metals to illustrate the above remarks and set the general picture. The characteristic, common features of their band structures at equilibrium are well known. The filled[3] d bands are crossed by and hybridize with a NFE sp band containing approximately one electron distributed roughly equally over s and p states. The square-well pseudopotential V_0 for $l=0$ gives the bottom of the s band, i.e., it is close to the Γ_1 state. This lies 0.3 Ry (Ag) or 0.5 Ry (Cu, Au) below the center of the d bands. The value of V_l for the p states for all three metals is nearly the same as V_0, and with the masses τ_s and τ_p near unity, the sp band is genuinely NFE-like. The values of $\varepsilon_{xc}(S)$, at the respective equilibrium volumes are in the range -0.53 to -0.59 Ry. For all three metals one has, on an energy scale where $V(S)=\mu_{xc}(S)$, that $\langle E\rangle_1 > \langle E\rangle_0 > \varepsilon_{xc}(S) > V_0 \approx V_1$. From these general considerations it follows that $P_{t1}(s) \approx P_{t1}(p)$, both being large and negative. Obviously, $\langle E\rangle_l - V_l$ must be positive for $l=0$ as well as $l=1$. It then follows from (30b) and (30c) that P_{t2} and P_{t3} both must be positive for $l=0$ and $l=1$. Since the half-full NFE band consists predominantly of occupied bonding s and p states, we would expect the net sp pressure to be negative, i.e., that the negative P_{t1} for $l=0,1$ outweigh the positive $P_{t2}+P_{t3}$.

We can also make some general predictions for the d pressures. Since the d bands contain almost the nominal ten electrons, and as they are relatively narrow, $\langle E\rangle_2$ almost coincides with C_2. The d band center moves towards higher energies under compression. Thus, we would expect that $\delta C_2/\delta \ln S$ is negative, i.e., that $P_{c1}(d)$ in (29a) is positive. This agrees with the alternative second expression for $P_{c1}(d)$ in Eq. (29a), because we expect $\langle E\rangle_1 \approx \langle E\rangle_2 \approx C_2$, which combined with the ordering of characteristic energies given above, gives $C_2-[V(S)-\mu_{xc}(S)] > \varepsilon_{xc}(S)$. Thus the equation (29a) appears to yield a d-shell repulsive term with the proper sign. It is somewhat more difficult to predict even the signs of the two remaining contributions P_{c2} and P_{c3} to the central d pressure. We have already made general remarks about the bonding redistribution and hybridization. Since the d bands are relatively narrow, the bonding redistribution may not be very large and may be outweighed by hybridization. Since the d band is crossed by the sp band and the hybridization matrix element is proportional to k^2 (Ref. 27, p. 66), the d band will be pushed up a little near the center of the Brillouin zone and down by a larger amount in the outer parts of the Brillouin zone, thus giving a net depression of $\langle E\rangle_2$, i.e., negative $\langle E\rangle_2 - C_2$ and negative $P_{c2}(d)+P_{c3}(d)$. Incidentally, hybridization is the interaction of the d states with the $l=2$ component of the sp band which arises from expanding the tails of s and p orbitals about the centers of neighboring atoms. Thus hybridization does not mix different l in the strict sense, only in the loose sense that we refer to sp or d bands.

III. CALCULATED PRESSURES

We do not intend to present here the best possible local-density band-structure calculations for the noble metals. We use the linear muffin-tin orbital (LMTO) method,[29] but we stay within the simplest approximation, the ASA (atomic-sphere approximation).[37,38] We do not include the so-called "combined correction term" which corrects for the nonspherical shape of the cell and the omission of partial waves with $l > l_{\max}$. Most of the results presented here are derived with $l_{\max}=2$. However, in order to estimate errors introduced by this choice, which is made since it facilitates our analysis, some data where $l_{\max}=3$ will also be given. The actual choice of the number of angular momenta included will be given in each graph. Figure 2 illustrates, in the case of Cu, the effects on the total pressure of including f states. The LDA is known to give all atomic sizes a little too small and therefore for consistency we will discuss the calculated pressures in terms of the calculated equilibrium Wigner-Seitz radius S rather than the experimental one.

Numerical results for the pressure parameters for the noble metals are given in Tables I—III. Except as otherwise stated, energies will be expressed in rydbergs and distances in Bohr units (a.u.). We note general agreement about signs and orders of magnitude with the qualitative discussion at the end of Sec. II. We also see the approximate agreement between the exact P_l from (9) and (10) and the approximate P_l^a (29) and (30). We had expected the effect of sp-p hybridization to be mixed with other effects and spread between the P_{t2}, P_{t3}, P_{c2}, and P_{c3} for $l=0,1,2$ with substantial cancellations between them, as indeed the table demonstrates. Thus we cannot extract any net hybridization from the tables. However, we would like to verify that it is a substantial effect and have therefore chosen a different approach. In the LMTO-ASA method one can simply set to zero the matrix elements connecting the s and p bands with the d bands and

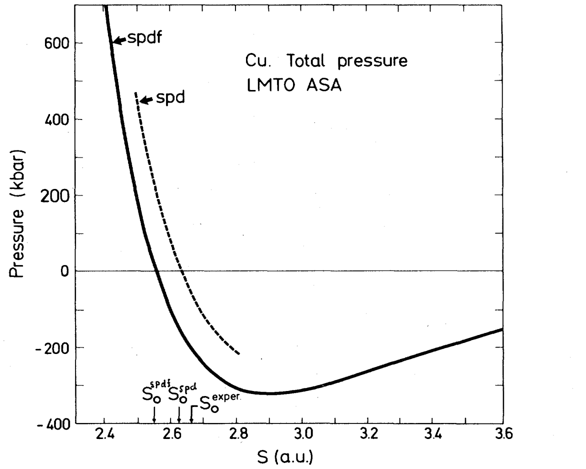

FIG. 2. Total pressure and equilibrium Wigner-Seitz radius S_0 using scalar relativistic, self-consistent LMTO-ASA for Cu. Solid curve and S_0 ($spdf$) for $l_{\max}=3$; dashed curve and S_0 (spd) for $l_{\max}=2$.

TABLE I. Potential parameters, partial pressures, and approximate pressure components for Cu at three different volumes. The approximate partial pressures P_l^a are calculated as $\sum_i P_{ti}(l)$ for s, p, and f states and as $\sum_i P_{ci}(l)$ for $l=2$ (d). The various parameters are all defined in the text (Sec. II).

S (a.u.)	2.400				2.551				2.750			
E_F (Ry)	0.0830				−0.0646				−0.1910			
$N(E_F)$ [(e/at.)/Ry]	3.4733				3.9060				4.4289			
$\varepsilon_{xc}(S)$ (Ry)	−0.6874				−0.6324				−0.5695			
P_{tot} (kbar)	641.7				0.0				−282.2			
l	s	p	d	f	s	p	d	f	s	p	d	f
$\langle E\rangle_l$ (Ry)	−0.4659	−0.2776	−0.2140	−0.2176	−0.5215	−0.3614	−0.3064	−0.3095	−0.5549	−0.4261	−0.3829	−0.3851
C_l (Ry)	−0.2841	0.9465	−0.1958	4.9828	−0.3872	0.7019	−0.2927	4.4272	−0.4670	0.4750	−0.3739	3.8270
μ_l	0.7663	0.8323	11.998	0.7187	0.8093	0.8638	14.212	0.7065	0.8690	0.9038	17.548	0.6927
V_l (Ry)	−0.8132	−0.8825	4.4008	−1.0359	−0.8340	−0.8759	3.2934	−0.9425	−0.8288	−0.8385	2.4553	−0.8377
τ_l	0.8431	0.9743	0.0416	1.0214	0.8768	0.9883	0.0452	1.0224	0.9222	1.0092	0.0436	1.0232
n_l (e/at.)	0.6796	0.8452	9.3864	0.0890	0.6898	0.7822	9.4548	0.0732	0.7040	0.6964	9.5422	0.0574
P_l (kbar)	306.3	339.4	92.8	−96.8	105.8	34.2	−70.7	−69.3	−9.6	−108.5	−119.9	−44.2
P_l^a (kbar)	301.8	355.4	60.5	−91.9	103.9	49.8	−66.8	−67.3	−9.3	−127.7	−97.8	−43.6
P_{c1} (kbar)	605.8		651.3		295.6		319.3		93.5		119.7	
P_{c2} (kbar)	−378.3		−763.4		−226.8		−469.4		−115.0		−246.8	
P_{c3} (kbar)	69.9		172.6		31.4		83.3		8.6		29.3	
P_{t1} (kbar)	−257.8	−716.6		−230.9	−334.3	−677.5		−140.5	−334.3	−552.5		−76.1
P_{t2} (kbar)	510.9	922.5		111.5	368.0	584.4		58.9	244.6	316.0		26.2
P_{t3} (kbar)	48.5	149.6		27.5	70.2	142.9		14.3	80.4	108.8		6.3

TABLE II. As Table I, but for silver.

S (a.u.)	2.800				2.912				3.000			
E_F (Ry)	−0.0501				−0.1362				−0.1875			
$N(E_F)$ [(e/at.)/Ry]	3.2155				3.4512				3.6863			
$\varepsilon_{xc}(S)$ (Ry)	−0.6125				−0.5765				−0.5500			
P_{tot} (kbar)	261.0				−3.6				−113.9			
l	s	p	d	f	s	p	d	f	s	p	d	f
$\langle E\rangle_l$	−0.5108	−0.3845	−0.4292	−0.4183	−0.5356	−0.4280	−0.4774	−0.4676	−0.5461	−0.4513	−0.5047	−0.4953
C_l (Ry)	−0.3786	−0.6522	−0.4276	3.2291	−0.4273	0.5188	−0.4768	3.0313	−0.4543	0.4336	−0.5052	2.8884
μ_l	0.7593	0.7779	7.9146	0.7865	0.7917	0.8001	9.029	0.7651	0.8179	0.8172	9.9870	0.7503
V_l (Ry)	−0.7697	−0.7465	−3.2175	−0.9553	−0.7760	−0.7492	−2.8167	−0.8898	−0.7737	−0.7428	−2.5330	−0.8424
τ_l	0.8407	0.9622	0.0924	1.0420	0.8670	0.9730	0.0985	1.0427	0.8879	0.9824	0.1052	1.0427
n_l (e/at.)	0.6782	0.7604	9.4414	0.1202	0.6808	0.7048	9.5132	0.1012	0.6834	0.6628	9.5650	0.0888
P_l (kbar)	79.2	84.8	211.8	−114.7	15.6	−21.7	88.2	−85.6	−15.6	−71.4	37.1	−74.6
P_l^a (kbar)	75.4	83.3	197.9	−111.1	12.8	−21.5	93.6	−84.0	−15.6	−70.6	52.9	−73.7
P_{c1} (kbar)	222.8		235.1		121.6		99.5		75.4		40.3	
P_{c2} (kbar)	−173.7		−41.6		−123.1		−6.3		−102.4		13.0	
P_{c3} (kbar)	24.7		4.3		12.9		0.4		7.6		0.4	
P_{t1} (kbar)	−202.9	−282.4		−189.6	−222.9	−296.7		−129.7	−223.4	−308.8		−106.3
P_{t2} (kbar)	240.5	322.3		56.3	191.0	229.7		33.1	160.3	191.3		23.8
P_{t3} (kbar)	37.8	43.4		22.3	44.7	45.5		12.6	47.5	46.9		8.8

TABLE III. As Table I, but for gold.

S (a.u.)	2.700				2.850				3.000			
E_F (Ry)	0.1626				−0.02831				−0.1705			
$N(E_F)$ [(e/at.)/Ry]	3.1511				3.6286				3.9436			
$\varepsilon_{xc}(S)$ (Ry)	−0.6908				−0.6340				−0.5879			
P_{tot} (kbar)	1228.2				292.5				−109.1			
l	s	p	d	f	s	p	d	f	s	p	d	f
$\langle E \rangle_l$ (Ry)	−0.5523	−0.3267	−0.2952	−0.2752	−0.6066	−0.4235	−0.3949	−0.3839	−0.6412	−0.4956	−0.4760	−0.4700
C_l (Ry)	−0.4763	0.8428	−0.2890	3.2503	−0.5582	0.6004	−0.3926	2.9649	−0.6124	0.4202	−0.4735	2.7204
μ_l	0.7554	0.7285	4.8220	0.8402	0.8085	0.7615	5.7414	0.8120	0.8659	0.7931	6.8455	0.7847
V_l (Ry)	−0.8994	−0.7270	−2.9609	−1.1102	−0.9162	−0.7686	−2.6490	−1.0061	−0.9168	−0.7731	−2.2927	−0.9198
τ_l	0.8347	0.9433	0.1913	1.0388	0.8778	0.9558	0.1815	1.0440	0.9233	0.9735	0.1907	1.0472
n_l (e/at.)	0.7762	0.9572	9.0410	0.2256	0.7876	0.8724	9.1628	0.1772	0.7988	0.7760	9.2858	0.1394
P_l (kbar)	115.2	440.0	869.0	−235.9	14.6	75.2	366.5	−163.8	−47.9	−78.4	129.1	−111.9
P_l^a (kbar)	148.5	428.0	735.6	−213.2	11.1	72.0	303.5	−155.9	−49.2	−78.8	102.8	−109.5
P_{c1} (kbar)	261.4		894.5		74.1		388.7		−19.3		135.0	
P_{c2} (kbar)	−128.8		−196.9		−68.5		−98.2		−32.2		−30.1	
P_{c3} (kbar)	15.6		38.0		3.6		13.0		−0.7		2.1	
P_{t1} (kbar)	−347.3	−111.4		−488.5	−384.9	−311.9		−287.9	−369.7	−330.3		−172.2
P_{t2} (kbar)	415.2	523.5		186.3	297.0	338.3		90.1	215.2	204.6		43.4
P_{t3} (kbar)	80.6	15.9		89.0	99.0	45.6		41.9	105.3	46.9		19.4

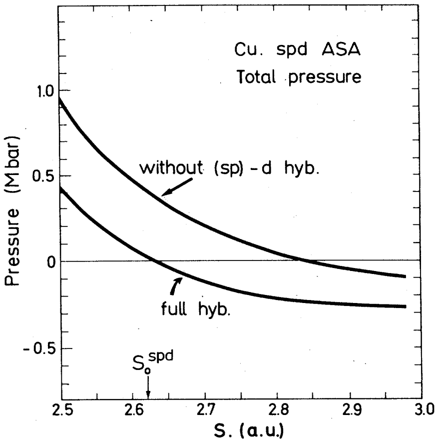

FIG. 3. Self-consistent, scalar-relativistic LMTO-ASA calculations for Cu, including s, p, and d partial waves. The calculated total pressure with full hybridization and that without (sp)-d hybridization are shown as functions of the Wigner-Seitz radius S. The theoretical equilibrium volumes correspond to those values of S for which the pressure is zero.

repeat the whole self-consistent calculation. This is not a very satisfactory procedure, as discussed further below, but we believe it gives qualitatively correct trends. The results for the total pressure for Cu are included in Fig. 3, which shows indeed a contraction of atomic radius from 2.84 to 2.63 due to hybridization. Similar results (not shown) were obtained for Ag and Au.

Details of the separate components of the central d pressure $P_{c1}(d)$, $P_{c2}(d)$, and $P_{c3}(d)$ for Cu are shown in Fig. 4 and have the general signs and relative magnitudes anticipated at the end of Sec. II B. In accordance with the discussion there, we focus on $P_{c1}(d)$ as the best measure we have of the pure full d-shell interaction without sp-d

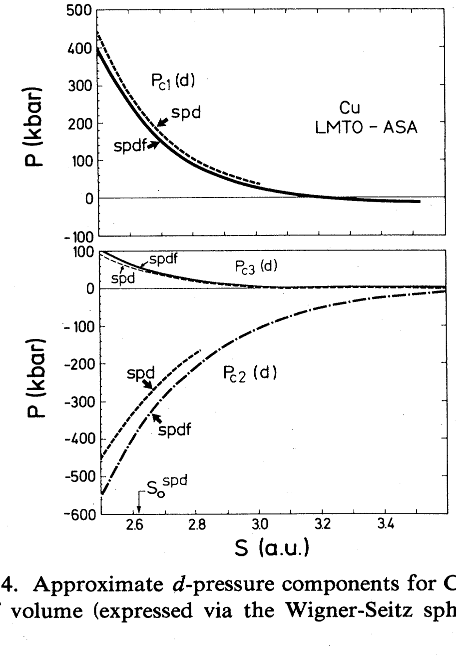

FIG. 4. Approximate d-pressure components for Cu as functions of volume (expressed via the Wigner-Seitz sphere radius S).

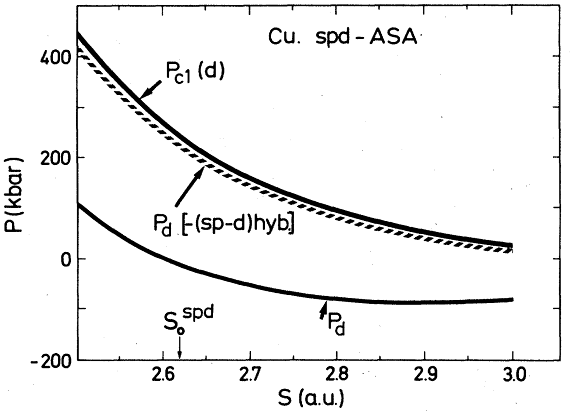

FIG. 5. $P_{c1}(d)$ and full d partial pressure P_d versus Wigner-Seitz radius S for Cu. Also shown (dashed curve) are the d partial pressures calculated without (sp)-d hybridization.

hybridization, i.e., what the interaction between the d shells would be if the d band were isolated and all other bands so far away that hybridization with them were negligible (Fig. 5). The $P_{c1}(d)$ is seen to be quite strongly repulsive around the equilibrium atomic-sphere radius, becoming very weakly attractive at much larger S, in accordance with the van der Waals interaction in the sense of Sec. I. We note that $P_{c1}(d)$ in fact is rather more weakly attractive than we would expect from the magnitude of the van der Waals interaction estimated by Richardson and Mahanty,[13] and suggest that the hybridization effect may be stronger and the van der Waals energy weaker than obtained by these authors. Similar results for $P_{c1}(d)$ were calculated for Ag and Au (Figs. 6 and 7).

In order to get an independent estimate of the pure d-shell interaction we performed the calculations already mentioned with the sp-d hybridization matrix elements switched off (but the s to p matrix elements retained). The pure d-shell interaction should then correspond to the full d pressure in the unhybridized calculation, and this is shown for Cu, Ag, and Au in Figs. 5—7 to be compared with $P_{c1}(d)$ (not P_d) for full hybridization. For Cu the two agree remarkably: for Ag and Au the unhybridized calculations follow the same general curve as $P_{c1}(d)$ but about 100 kbar even more repulsive. The trouble with these unhybridized calculations is that they give rather peculiar bands. The pressure formulas assume self-consistency in the bands, and these were therefore recalculated completely in the unhybridized scheme. For Ag the top of the d band lay just below the Fermi level E_F, for Cu and Au slightly above, thus introducing a few real holes. In view of these problems, it is gratifying that the unhybridized calculations give a pure d-shell interaction broadly similar to the $P_{c1}(d)$ which we prefer. Incidentally, if one (incorrectly) uses non-self-consistent bands calculated without hybridization from the with-hybridization potential, one still obtains a substantial pure d-shell repulsion but about 100—200 kbar less than $P_{c1}(d)$.

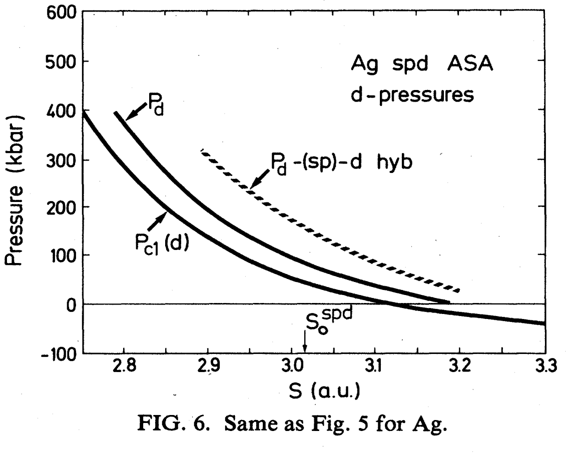

FIG. 6. Same as Fig. 5 for Ag.

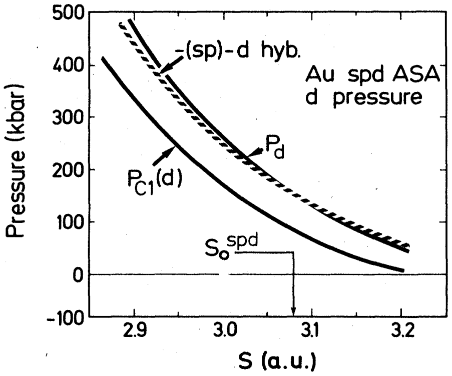

FIG. 7. Same as Fig. 5 for Au.

To complete the picture we analyze the tail pressures for $l=0$ and 1, representing the NFE gas of sp electrons. The kinetic (Fermi) pressures for a noninteracting free-electron gas of one electron at the calculated radii are 418, 207, and 188 kbar for Cu, Ag, Au, which are seen to be nearly half of $P_{t2}+P_{t3}$ for $l=0$ and 1 combined, which we shall call $P_{t2,3}(sp)$. The remaining half is due to hybridization and cancels a corresponding negative hybridization contribution to $P_{c2}+P_{c3}$ as already remarked. Alternatively, we can say that the total number n_0+n_1 of sp electrons is around 1.5 (Tables I-III) due to hybridization and that the kinetic pressure of an electron gas of this density accounts for almost all of $P_{t2,3}(sp)$. This quantity is therefore behaving as expected, which gives us confidence in carrying the same analysis forward to $P_{t1}(sp)$. This should contain the exchange and correlation pressure for a free-electron gas with Coulomb interactions, namely, about -220, -130, and -120 kbar for Cu, Ag, and Au, leaving a large negative part of $P_{t1}(sp)$ to be ascribed to the very attractive pseudopotentials, which is consistent with the large negative V_0 and V_1.

This large negative $P_{t1}(sp)$ is basically what balances the positive pure d-shell repulsion. The variation of $P_{t1}(s)$ and $P_{t1}(p)$ with radius is shown in Fig. 8 and we can interpret it in terms of the pseudopotential[39—41] $V_{ps}(r)$ depicted for $l=0$ for Au in Fig. 9. We note that $V_{ps}(r)$ is very attractive at -0.8 Ry around $r=2$ to 3 (Fig. 9) compared with potassium which has the same core radius, which gives the large negative V_0 and V_1 and large negative $P_{t1}(sp)$. However, as the Wigner-Seitz radius S is reduced, the sp electrons get squeezed increasing-

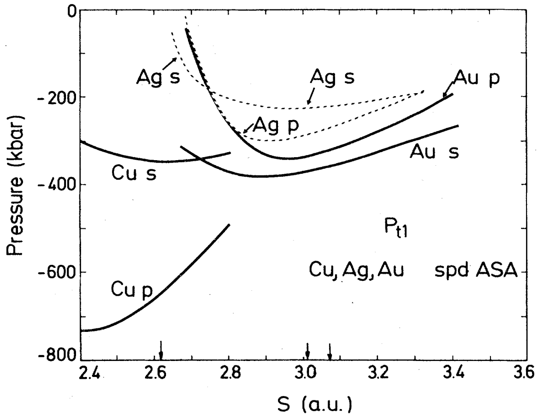

FIG. 8. P_{t1} components of the "tail pressures" of the noble metals. (Arrows indicate S_0^{spd} for Cu, Ag, and Au.)

ly into the repulsive part of the pseudopotential at small r (Fig. 9), making P_{t1} go up until it ultimately becomes repulsive (Fig. 8).

Finally, we comment on some differences between the noble metals. It had at one time been thought that Cu and Au should be similar, with Ag having a significantly tighter d shell because of its lying deeper below E_F, as evidenced by the colors of the three metals. No doubt there must be some such effect which may account for the smaller P_d for Ag at equilibrium compared with Cu and Au. However, in most respects, e.g., Fig. 8, Cu differs markedly from Ag and Au. This is easily understood in terms of the pseudopotentials seen by the d-shell electrons and the radii of their orbitals. For Cu there is no deeper $l=2$ shell so that the electrons see the full potential, whereas in Ag and Au the inner part is cancelled out in the sense of the pseudopotential cancellation theorem.[41,42] In consequence, the maxima of the d orbitals occur at $r=0.6$, 1.2, and 1.2, respectively, leading to a larger d charge density at the Wigner-Seitz radius and a larger hybridization matrix element in Ag and Au than in copper (p. 66 of Ref. 27).

IV. DISCUSSION

We now discuss further the physical interpretation and physical consequences of the results of Sec. III. The three salient features emerging from our analysis of the partial pressures were a strongly positive pure d-shell repulsion, balanced by a net negative hybridization pressure and a negative sp NFE pressure. The last is due to the attractive $l=0$ pseudopotential sucking the electron gas inwards, an effect that has been demonstrated directly by the charge redistribution calculations[43,44] for CsAu where the electron transferred from Cs was relocated in the radius range 1.9–2.5 a.u. on the gold atom. (For comparison, the Wigner-Seitz radius of Au is 3.0 a.u.) It was also shown that the extra gold electron density is mostly of s character, which correlates[20] with the shape of the gold $l=0$ pseudopotential being anomalously attractive in just the range mentioned (Fig. 9). The reason for the anomalous shape of the Au^+ $l=0$ pseudopotential compared with that of K^+ is connected with the soft d shells as discussed elsewhere,[20,41,42] that for $l=1$ being more normal.

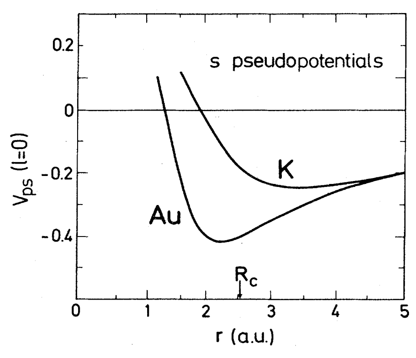

FIG. 9. Pseudopotentials in hartrees (double rydbergs) corresponding to $l=0$ for Au^+ and K^+ (after Ref. 39).

In order to make physical arguments relating to alloys and surface reconstruction of the noble metals in the sense of Sec. I, we need to know or assume how the three effects above behave in the presence or absence of neighboring atoms. The pure d-shell repulsion (without hybridization effects) we take to be predominantly a pairwise interaction between d shells in contact, vanishing at a free surface and in alloys where the d shells are kept out of contact. The NFE pseudopotential attraction we refer to as a volume (one-atom) effect ("volume force" for short): the interaction energy is the product of the atomic pseudopotential and the NFE sp-electron density, the latter broadly determined by the atomic density in a region, in a sense by the volume available to the one gold sp electron.

The less obvious assignment is the sp-d hybridization as also predominantly a volume and (one-atom) force different from the pure d-shell repulsion (which was the purpose behind our careful analysis of the partial pressures). We will not go into all the details of pseudopotential[41,42] and hybridization theory[45,46] but regard it as evident enough that sp-d hybridization in our context is the interaction of the d electrons on one atom with the $l=2$ component of the sp NFE wave functions on that atom: note, for example, the hybridization matrix element as an *intra*-atomic integral (p. 66 of Ref. 27). The hybridization for a NFE state with wave vector $\mathbf{k}$ and energy above or below the d band gives an additional effective pseudopotential

$$V_{\mathbf{k}} \propto \sum_{m=1}^{5} \frac{\gamma_{\mathbf{k}m}^{*}\gamma_{\mathbf{k}m}}{E(\mathbf{k})-E_{dm}(\mathbf{k})}\,, \tag{31}$$

where $\gamma_{\mathbf{k}m}$ is the hybridization coupling to the mth d band. Thus, $V_{\mathbf{k}}$ is predominantly a one-atom pseudopotential which depends only weakly on neighboring atoms through the energy dispersion $E_{dm}(\mathbf{k})$ of the d band. To obtain the total hybridization energy in the system requires summing its effect on the occupied d shells and NFE states below E_F. The interaction is very complicated where the bands cross but we can perform the summation by noting from the trace invariance of a Hamiltonian matrix that the total hybridization energy would be zero if summed over the d bands and all NFE bands up to infin-

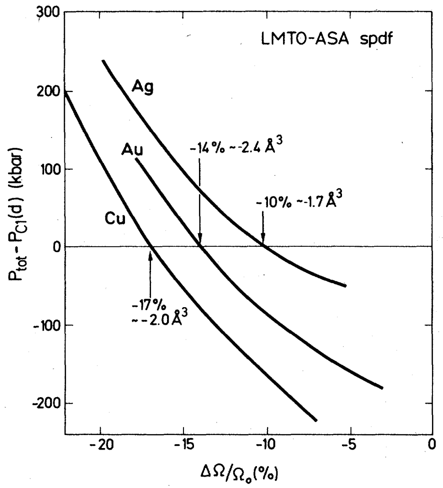

FIG. 10. Calculated difference, $P_{\text{tot}} - P_{c1}(d)$, between the total pressure and the repulsive d-shell term for Cu, Ag, and Au as functions of the relative volume deviation from (theoretical) equilibrium.

ite energy. Thus our summation up to E_F is the negative of the summation from E_F to infinity where the form (31) applies. This establishes the combined effect of hybridization on the d shells and the occupied sp states as also predominantly a one-atom (volume) effect. We believe the above interpretation is fully supported by more detailed theories of noble-metal cohesion,[45–47] though these do not address quite the same issues of the pairwise or other nature of the forces.

We have argued that the approximate pressure component $P_{c1}(d)$ given in Eq. (29a) (for $l=2$) represents the pairwise repulsive interaction between the d shells. We wish here to substantiate this assignment further by applying our model to compute the "noble-metal contraction" observed by Nevitt[22,23] and others[48] for the MN alloys, i.e., we shall calculate the difference $\Omega_N^* - \Omega_N$ referred to in Sec. I. If our understanding of $P_{c1}(d)$ is correct, then we should obtain Ω_N^* simply as the volume at which the total pressure P_{tot} minus $P_{c1}(d)$ vanishes (Ω_N is, of course, the volume at which $P_{\text{tot}}=0$). The result follows from Fig. 10, where the calculated values of $P_{\text{tot}} - P_{c1}(d)$ are shown for Cu, Ag, and Au. The relative volume contractions which we find, are for Cu, Ag, and Au, 17%, 10%, and 14%, corresponding to $\Delta\Omega = \Omega_N^* - \Omega_N = -2.0$ Å^3 (Cu), -1.7 Å^3 (Ag), and -2.4 Å^3 (Au). These results agree well[38] with those obtained from the analysis of the data given by Nevitt,[22,23] -1.8, -1.2, and -3.0 Å^3.

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[4] We further mention that the elastic shear moduli exhibit trends similar to those observed for B. It is possible, in first-principles calculations (see Ref. 30) to separate a band-structure term and an electrostatic contribution to the elastic constants. The band-structure part alone also shows the trends as given by Fig. 1 here [N. E. Christensen, ψ_k Newsletter **8**, 2 (1984)].

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[35] Note that the potential functions enter the atomic-sphere-approximation—Korringa-Kohn-Rostoker (ASA-KKR) secular equations, which given the band structure, as

$$\sum_{l',m'} [S^{\mathbf{k}}_{lm;l'm'} - \mathscr{P}_l(E)\delta_{ll'}]\chi_{l'}(E,S)B^{\mathbf{k}}_{l'm'} = 0 ,$$

where $\underline{S}^{\mathbf{k}}$ are the structure constants (Ref. 29). The *pure l* band $E_{li}(\mathbf{k})$ is obtained from $\mathscr{P}_l(E_{li}(\mathbf{k})) = S^{\mathbf{k}}_{li}$, where $S^{\mathbf{k}}_{li}$ is the diagonalized l subblock (canonical band) of the structure-constant matrix. The canonical band has its center at $S=0$. The top is close to $S=2(2l+1)$ and the bottom to $S=-(2l+1)(l+1)/l$, which gives the Wigner-Seitz rules (Refs. 26 and 29).

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