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Parametrized version of the generalized pseudopotential theory for noble metals: Application to copper

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A parametrized version of the generalized pseudopotential theory (GPT) of Moriarty is proposed for the special case of the noble metals. Copper is taken as an example. To define the parametrization, we consider separately the contributions which in the GPT are defined as the simple-metal limit (SML), the s-d coupling, and the overlap. The perturbation expansion is done from the basis of the atomic d states, and the d bands of the noble metal are considered to be completely filled. The SML is represented as an empty-core potential of radius r_c, and the s-d—coupling calculation is done exactly, but the mean energy E_d of the d band relative to the conduction band is considered to be adjustable. The two parameters r_c and E_d are determined from particular points of the band structure. The results are found to be consistent with the large-L band-gap value and the width of the resonance of copper. The SML of the form factor, and the total form factor obtained, are in good agreement with those of the *ab initio* GPT. By means of the optimized random-phase approximation, we analyze the influence of the overlap on the liquid structure. We find that the expression for the overlap pair potential of Moriarty gives a good estimation of the liquid structure factor. Conversely, this quantity is used to adjust the overlap pair potential. Further concluding tests of the parametrization are done by calculating the entropy C_V, the compressibility, and the resistivity of the liquid. It is found that the parameters r_c, E_d, and those of the overlap are almost insensitive to volume changes with temperature in the solid and liquid under normal pressure. We conclude that the parametrized approach gives a good picture of the electron-ion and interionic interactions without losing the essence of the GPT. The method cannot replace the *ab initio* calculation, but could be useful in the investigation of noble-metal properties in systems which are not easily tractable in a detailed theory.

I. INTRODUCTION

The extension of the pseudopotential theory of simple metals in order to include the effects of the transition-metal d bands has received considerable attention over the past decade.[1-4] The transition series end with the noble metals, which have a maximum electron occupation in the d bands. Copper, silver, and gold, in particular, have been studied by Moriarty[2,5,6] and Dagens[7,8] in a series of works in which they, respectively, extend to the noble metals the well-known schemes of the orthogonal-plane-wave (OPW) pseudopotential and the resonant model potential.

In the first approach, Moriarty has considered the OPW expansion supplemented by an expansion on the basis of the atomic d states. The most recent version of Moriarty's generalized pseudopotential theory (GPT) connects the pseudoatom approach and the density-functional formalism.[9,10] In the case of the noble metals, Moriarty has shown that the assumption of a completely filled d band leads to difficulties and has proposed possible improvements.[2]

Dagens's resonant model potential (RMP) avoids some of the difficulties which are encountered in the GPT, owing to a parametrization procedure. There are several ways to accomplish this parametrization; for instance, by fitting the band-structure data[7] or by matching the screened RMP to the Hartree-Fock-Slater self-consistent potential.[8] Some of the advantages of the RMP are due to the fact that the simple-metal contribution and the resonant part of the model are well separated. From Dagens's work it is clear that the simple-metal contribution to the potential can be described using a standard model potential, either local or nonlocal, depending on the degree of refinement which is sought. The important originality of the model lies in the resonant part, which is constructed with the assumption of ultralocalized d wave functions so that no overlap occurs between the wave functions of neighboring ionic sites. Such a procedure by-passes the intricate overlap calculations which have to be done in the case of the GPT. Nevertheless, it seems more difficult to find a parametrization of the RMP which rigorously agrees with the nonoverlapping condition in the liquid state.

Many attempts using a simpler scheme have been proposed in the literature to avoid the lengthy calculations which are associated with the GPT and RMP. Unfortunately, such simple approaches conceal the physics of the d-electron behavior. An intermediate theory has recently emerged with the work of Wills and Harrison on the interionic interactions in transition metals.[11] To describe the trends in the transition-metal series, these authors show that a two-parameter model can be convenient.

One parameter is the radius r_c of the empty-core model which characterizes the interactions of the conduction electrons with the bare ions. The second parameter is an effective d-state radius r_d which is obtained from the d-d coupling between neighboring sites. Moreover, the value of r_d is mainly a characteristic of the free atom rather than that of the d band itself. The pseudopotential of Wills and Harrison belongs to the class of the semiempirical models often invoked by Heine,[12] and is transferable to different physical contexts provided that r_c and r_d are somewhat adjusted. Although we are not concerned with the tight-binding approach, it may be useful to underline that Pettifor[13,14] has developed a hybrid-NFE-tight-binding model Hamiltonian (where NFE denotes nearly free electron), and has pointed out that the description of the structure trends across the transition series necessitates only two d-resonance parameters.

Although very different, the approaches of Wills and Harrison and Pettifor have an important common feature: both need only a small number of parameters to reproduce the transition-metal properties. We believe that a parametrization procedure can also be useful in the framework of the GPT or the RMP.

The main purpose of this paper is to show that besides the full *ab initio* GPT, such a simple parametrization can be reached by considering separately the three principal contributions of the GPT which are, respectively, associated with the free-electron-like states, the s-d coupling, and the overlap. To do this, we shall by-pass most of the detailed charge-density calculations in using the band-structure data for the two first contributions and considering properties depending on interionic interactions to adjust the overlap contribution.

In a previous paper[15] we showed that the determinations of the GPT and RMP at the solid-state density are good starting points to investigate the disordered state. Since we are mainly interested in the liquid state, the results of our parametrized GPT will be principally compared to experiments concerning the liquid properties. The parametrization procedure could be applied to all noble metals, but in the following it will be developed only for copper, since its band-structure data[16–18] as well as many measurements of its liquid properties have been extensively investigated.

This paper is arranged as follows. In Sec. II we present the main quantities of interest for a parametrized GPT and discuss the adjustment procedure for the simple-metal and s-d—coupling contributions. In Sec. III we derive the pair interionic interactions and discuss the adjustment of the overlap contribution. In Sec. IV we calculate various structural, thermodynamical, and transport properties. The comparison to the previous *ab initio* approaches of the GPT or RMP is done when necessary throughout this work.

II. PARAMETRIZATION OF THE GPT FORM FACTOR

The essence of the GPT lies in the fact that the small-core approximation is no longer valid for the d states which are not exact eigenstates of the crystal Hamiltonian and which form bands which hybridize with the nearly-free-electron band. To determine the energy of these bands, we must calculate the extra potential $-\delta V$ "seen" by a d electron when going from the free atom to the metal, and the hybridization operator Δ which is defined by[1,5]

$$\Delta = \delta V\,|d\rangle - \langle d\,|\,\delta V\,|\,d\rangle\ . \tag{1}$$

The simple-metal pseudopotential form factor can be extended to the transition metal, and the new expression reads[1,5]

$$\begin{aligned} w(\vec{k},\vec{q}) = {} & \Big\langle \vec{k}+\vec{q}\,\Big|\, v + \sum_{\alpha} (E_k - E_\alpha)\,\Big|\alpha\Big\rangle\langle\alpha\,|\,\vec{k}\rangle \\ & + \Big\langle \vec{k}+\vec{q}\,\Big|\sum_{d} (\,|d\rangle\langle\Delta| + \Delta\,|d\rangle\langle d|\,)\Big|\vec{k}\Big\rangle \\ & + \Big\langle \vec{k}+\vec{q}\,\Big|\sum_{d} \frac{\Delta\,|d\rangle\langle d\,|\,\Delta}{E_k - E_d}\Big|\vec{k}\Big\rangle\ , \end{aligned} \tag{2}$$

where $E_d = \langle d\,|\,T+V\,|\,d\rangle$ is the mean d-band energy relative to the minimum energy of the free electron, and $E_k = k^2/2$ is the free-electron kinetic energy (all relations given throughout the text are given in the atomic-unit system, i.e., with $e = \hbar = m = 1$).

In relation (2) v is the single-site contribution to the total self-consistent potential V in the metal. The $|\alpha\rangle$ correspond to the core states including the basis set of d states chosen for the calculation.

Several important changes have been introduced in the last GPT development of Moriarty.[2] These changes improve or optimize the formalism through the elimination of large cancellations between terms. Thus we note the following.

(i) The difference in the exchange potential when going from the free atom to the metal is not assumed to be a constant, but is taken as $\vec{r}$ dependent.

(ii) The potential due to the charge distributions of the neighboring ions in the metal is not spherically averaged. Thus, the extra potential V can be separated into volume- and structure-dependent parts: $\delta V = \delta V^{\mathrm{vol}} + \delta V^{\mathrm{struc}}$.

(iii) The orthogonalization-hole distribution $n_{\mathrm{OH}}(\vec{r})$ is not the usual simple-metal definition $n^0_{\mathrm{OH}}(\vec{r})$, and includes the orthogonalization-like nature of one of the hybridization contributions. It is now defined by

$$n_{\mathrm{OH}}(\vec{r}) = n^0_{\mathrm{OH}}(\vec{r}) - \frac{2\Omega}{(2\pi)^3}\int_{k>k_F} h_2(\vec{k},\vec{r})\,dk\ , \tag{3}$$

where the function $h_2(\vec{k},\vec{r})$ is given by Eq. (22) of Ref. 2.

These modifications are basic improvements of the earlier theory,[5,6] and, moreover, allow a computationally efficient representation of the principal quantities, i.e., the form factor, the energy-wave-number characteristic, and the overlap potential. This last development of the GPT (Ref. 2) applies very well to the simple metals and to metals which, respectively, correspond to the empty- and filled-d-band limits of the GPT. However, in the case of the noble metals, the filled-d-band limit seems inadequate because the hybridization empties out about 0.5 electron per atom from the d band, a value which is not small when compared to the chemical valence $Z=1$ of the noble elements. To improve the GPT for the noble metals, Moriarty has suggested either a rigorous reformulation or an *ad hoc* adjustment of the GPT formalism. In the first case, the GPT is modified by allowing the d states to unfill and a self-consistent valence to be achieved in zero order. In the second case, the filled-d-band scheme is conserved, but an adjustable core shift is introduced. Here we shall explore the route of parametrization. We use the expansion on the basis of the atomic d states rather than pseudoatom d states, and we include the previously mentioned changes. Therefore, the terms involved in cases (i)—(iii) differ from those of Moriarty and will be detailed in the next sections. Since we start from a delocalized d-state basis, we expect a good electron density and band structure in the noble metals, but, on the other hand, we do not expect that the criteria $\delta V^{\mathrm{vol}} \gg \delta V^{\mathrm{struc}}$ will be well satisfied, as discussed in Ref. 2. To avoid this difficulty, we must consider the mean d-band energy as an adjustable parameter.

A. Simple-metal limit

The simple-metal limit (hereafter denoted SML) of the form factor is immediately obtained from (2) when $\Delta=0$. It is well known that in many s-p metals, a simple way to obtain the form factor is to start from the crude but successful Ashcroft empty-core model $w_A=-(Z/r)\Theta(r-r_c)$. Θ is the Heaviside step function and r_c is the model radius which is close to the ionic radius.[19] Therefore we suggest that the form factor (2) can be simplified by modeling the SML using the empty-core potential. In using this assumption in the case of noble metals, we admit that the effects associated with the orthogonalization hole, the nonlocality, and the partial cancellation[20] inside the core can be all modeled from w_A, provided that the radius r_c is suitably adjusted. Such a representation of the SML may seem oversimplified. However, we observe that Dagens has found it convenient to represent the SML of the RMP from the local model potential of Shaw,[7] and that Wills and Harrison also consider the ion—free-electron interaction in transition metals by means of the empty-core model. Using this model in the first term of (2), the form factor can be written as

$$w(\vec{k},\vec{q})=w_A(q)+v_s(q)+w_B(\vec{k},\vec{q})+w_R(\vec{k},\vec{q})\ , \tag{4}$$

where $w_A(q)$ is the Fourier transform of the empty-core bare-ion pseudopotential. $w_B(\vec{k},\vec{q})$ and $w_R(\vec{k},\vec{q})$ are, respectively, the last two terms of (2). $v_s(q)$ is the part of the Fourier transform of $v(r)$ that has not been included in $w_A(q)$. After straightforward calculations, the form factor can be written as

$$w(\vec{k},\vec{q})=\frac{1}{\epsilon^{\mathrm{xc}}(q)}\left[w_A(q)+\frac{4\pi}{q^2}[1-G(q)][n_{\mathrm{OH}}(q)+\delta n_s(q)]\right]+w_B(\vec{k},\vec{q})+w_R(\vec{k},\vec{q})\ , \tag{5}$$

where

$$\epsilon^{\mathrm{xc}}(q)=1-\frac{4\pi}{q^2}[1-G(q)]\chi\left[\frac{q}{2k_F}\right]\ , \tag{6}$$

with

$$\chi(x)=-\frac{k_F}{\pi^2}\left[\frac{1}{2}+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right]\ .$$

Here, we represent the local-field exchange-correlation function $G(q)$ by the approximate Vashista-Singwi relation.[21] The comparison of this local-field approximation with others has been done by Singwi and Tosi.[22] In expression (5), $n_{\mathrm{OH}}(q)$ is the Fourier transform of $n_{\mathrm{OH}}(r)$ given in (3). Owing to the use of the local model for the SML, the "orthogonalization-hole" density reduces to the second term of (2). We can write

$$n_{\mathrm{OH}}(q)=\frac{1}{4\pi^3}\int_{k>k_F}d\vec{k}\sum_d\Bigg[\langle d\,|e^{-i\vec{q}\cdot\vec{r}}|\,d\rangle\Bigg[\frac{\langle\vec{k}\,|d\rangle\langle d\,|\Delta|\,\vec{k}\rangle+\langle d\,|\Delta|\,\vec{k}\rangle\langle\vec{k}\,|d\rangle}{E_d-E_k}-\frac{\langle\vec{k}\,|\Delta|\,d\rangle\langle d\,|\Delta|\,\vec{k}\rangle}{(E_d-E_k)^2}\Bigg]$$
$$-\frac{2\langle\vec{k}+\vec{q}\,|d\rangle\langle d\,|\Delta|\,\vec{k}\rangle}{E_d-E_k}\Bigg]\ . \tag{7}$$

The function $\delta n_s(q)$ appearing in (5) is the contribution of the s-d coupling to the screening charge, given by

$$\delta n_s(q)=\frac{1}{2\pi^3}\int_{k<k_F}d\vec{k}\,\frac{w_B(\vec{k},\vec{q})}{E_k-E_{k+q}}-\frac{1}{2\pi^3}\int_{k>k_F}d\vec{k}\,\frac{w_R(\vec{k},\vec{q})}{E_k-E_{k+q}}\ . \tag{8}$$

The first term of Eq. (5), $w_A/\epsilon^{\mathrm{xc}}$, is the SML contribution to the form factor, which here is reduced to the standard local expression. In (5) we have clearly separated this contribution from all those remaining which come from the s-d coupling, which we now consider.

B. s-d coupling

The s-d—coupling contribution to the form factor is very important in the noble metals.[5] For instance, it is responsible for the large band gap at the L point of the Brillouin zone which is given by

$$L_1^u - L_2' = 2w(\vec{k}_L, -2\vec{k}_L)\,, \tag{9}$$

where $-2\vec{k}_L$ corresponds to the primitive translation in reciprocal space in the [111] direction. This gap is about 0.2 a.u. in copper, and only 0.01 a.u. in prototype s-p metals such as Mg and Al.[23] Therefore the s-d—coupling contribution must be examined carefully.

For a given choice of the d-state basis, the s-d coupling depends on the extra potential $\delta V(\vec{r})$ centered on each site. In the following the origin $\vec{r}=\vec{0}$ is arbitrarily located at the site i. It is important to note that there are several ways to separate $\delta V(\vec{r})$ into $\delta V^{\mathrm{vol}}(\vec{r})$ and $\delta V^{\mathrm{struc}}(\vec{r})$ components, but that, in the GPT, $\delta V^{\mathrm{vol}}(\vec{r})$ must be 1 order of magnitude larger than $\delta V^{\mathrm{struc}}(\vec{r})$ to develop tractable expansions.

From the general expression of the self-consistent potential and our choice of d-state basis, a natural separation of $\delta V(\vec{r})$ is the following:

$$\delta V^{\mathrm{vol}}(r) = v_{4s}(r) - \left[V_{\mathrm{unif}}(r) + \sum_{j\neq i} \frac{1}{r_j} \right] + \Delta\mu_{\mathrm{xc}}\,,$$

where

$$\Delta\mu_{\mathrm{xc}} = \mu_{\mathrm{xc}}(n_{\mathrm{core}}+n_{4s}) - \mu_{\mathrm{xc}}(n_{\mathrm{core}}+n_{\mathrm{unif}})\,, \tag{10}$$

and

$$\delta V^{\mathrm{struc}}(\vec{r}) = -\sum_{j\neq i} \left[v_{\mathrm{nuc}}(|\vec{r}_j-\vec{r}|) + v_{\mathrm{core}}(|\vec{r}_j-\vec{r}|) - \frac{1}{r_j} + v_{\mathrm{xc}}(|\vec{r}_j-\vec{r}|) \right] + \frac{1}{N} \sum_{\vec{q}\neq\vec{0}} \sum_j e^{i\vec{q}\cdot(\vec{r}-\vec{r}_j)} \frac{4\pi}{q^2} [1-G(q)][n_{\mathrm{OH}}(q)+n_s(q)]\,. \tag{11}$$

These two relations are written in the notation of Ref. 2 and contain the local densities corresponding to the core state $n_{\mathrm{core}}(r)$, to the valence electron in the free atom, $n_{4s}(r)$, and to the uniformly distributed valence charge in the metal, n_{unif}. The potentials v_{core}, v_{4s}, and V_{unif} are, respectively, those associated to these three previous densities. v_{nuc} is the nuclear charge density and v_{xc} is the difference:

$$v_{\mathrm{xc}} = \mu_{\mathrm{xc}}(n_{\mathrm{core}}+n_{\mathrm{unif}}) - \mu_{\mathrm{xc}}(n_{\mathrm{unif}})\,, \tag{12}$$

where μ_{xc} is the effective exchange-correlation potential that is calculated using Kohn-Sham exchange and the Singwi-Tosi interpolation scheme for the correlation energy.[22] It is expressed by the functional

$$\mu_{\mathrm{xc}}(n) = -0.984 n^{1/3} - 0.005\,98 \frac{1+9.43 n^{1/3}}{(0.0795+n^{1/3})^2}\,. \tag{13}$$

In Eq. (11), N is the number of ions and $n_s(q)$ is the Fourier transform of the total screening charge:

$$n_s(q) = 2[w_A(q)+v_s(q)]\chi(q) + \delta n_s(q)\,. \tag{14}$$

We have introduced the term $\sum_{j\neq i}(1/r_j)$ in Eqs. (10) and (11) so that we can write

$$V_{\mathrm{unif}}(r) + \sum_{j\neq i} \frac{1}{r_j} = V(0) - \frac{r^2}{2r_{\mathrm{WS}}^3}\,, \tag{15}$$

where r_{WS} is the Wigner-Seitz radius. The potential $V(0)$ on the site i is the Coulomb potential due to all the j ions and the uniform compensating background. To a good approximation, it is given by the constant $V(0) = 1.5/r_{\mathrm{WS}}$.

The assumption that $\delta V^{\mathrm{vol}}(\vec{r})$ exerts a larger influence than $\delta V^{\mathrm{struc}}(\vec{r})$ means that the strength of the s-d coupling is principally determined by the passage of a $4s$-localized density in the atom to a uniform density in the metal.

In this work the atomic d-state basis is obtained from the Roothan-Hartree-Fock tables of the $4s^1 3d^{10}$ configuration.[24] The direct potential $v_{4s}(r)$ is derived by solving the Poisson's equation, and is simply expressed in terms of the radial part $R_{40}(r)$ of the $4s$ wave function:

$$v_{4s}(r) = \frac{1}{r} \int_0^r x^2 R_{40}^2(x)\,dx + \int_r^\infty x R_{40}^2(x)\,dx\,. \tag{16}$$

In Fig. 1 we have reported $\delta V^{\mathrm{vol}}(r) - \delta V(0)$ and the various contributions to this quantity. It is clear that the exchange-correlation contribution almost cancels the v_{4s} potential, so that the behavior of $\delta V^{\mathrm{vol}}(r)$ principally comes from the r^2 dependence of $V_{\mathrm{unif}}(r)$. Therefore, the assumption of a constant exchange-correlation contribu-

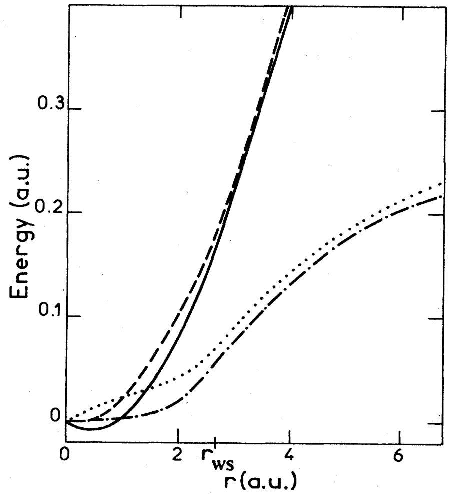

FIG. 1. Contributing terms to $\delta V^{\mathrm{vol}}(r)$. $v_{4s}(r) - v_{4s}(0)$: dotted line. $\Delta\mu_{\mathrm{xc}}$: dotted-dashed line. $r^2/2r_{\mathrm{WS}}^3$: dashed line. $\delta V^{\mathrm{vol}}(r) - \delta V(0)$: solid line. r_{WS} denotes the Wigner-Seitz radius.

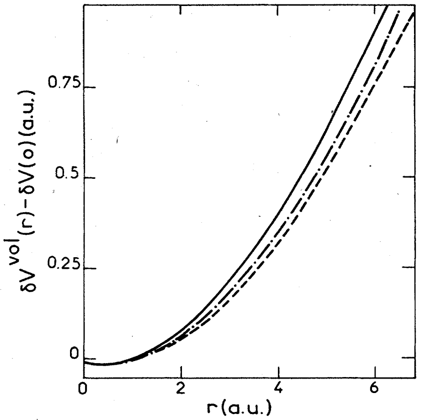

FIG. 2. Variation of $\delta V^{\rm vol}(r)-\delta V(0)$ with atomic volume. Solid at $T=0$ K, $\Omega=79.68$ a.u.: solid line. Liquid at $T=1356$ K, $\Omega=89.54$ a.u.: dashed-dotted line. Liquid at $T=1873$ K, $\Omega=93.44$ a.u.: dashed line.

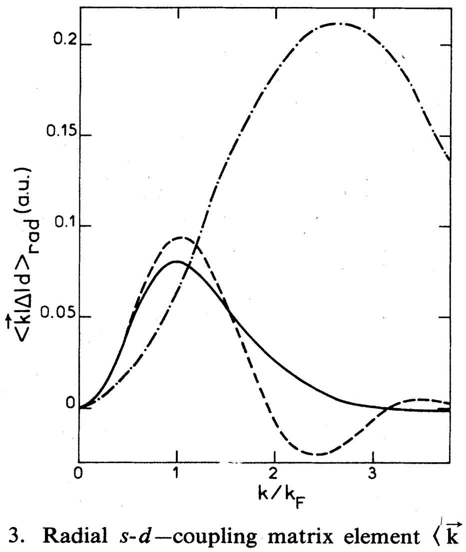

FIG. 3. Radial s-d—coupling matrix element $\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle_{\rm rad}$. Present calculation: solid line. Pseudoatom GPT: dashed line. RMP: dashed-dotted line. The GPT and RMP curves are taken from Fig. 8 of Ref. 2.

tion[5] underestimates $\delta V^{\rm vol}(r)$, mainly at distances close to or above the Wigner-Seitz radius.

Since we need the extra potential in the liquid state, we have examined in Fig. 2 the change of $\delta V^{\rm vol}(r)-\delta V(0)$ with volume by comparing the curves corresponding to the solid at the temperature 0 K and normal pressure, and to the liquid at the melting point (1356 K) and at the higher temperature of 1873 K. We remark that the curves do not deviate very much from a quadratic form. This fact is useful for obtaining convenient algebraic expressions for the s-d—coupling matrix elements and for saving computation time (see Appendix). A way to check our assumption that $\delta V(\vec{r})$ is principally defined by $\delta V^{\rm vol}(r)$ is to calculate $-\langle d\,|\,\delta V^{\rm vol}(r)\,|\,d\,\rangle$, since the shift from the atomic d energy level E_d^a is given by

$$E_d-E_d^a=-\langle d\,|\,\delta V(r)\,|\,d\,\rangle \ . \tag{17}$$

We find $E_d-E_d^a=0.165$ a.u., a value which is of correct magnitude when compared to that (0.280 a.u.) obtained by Hodges *et al.*[25] from their renormalized-atom approach. Nevertheless, the difference indicates that the criterion $\delta V^{\rm vol}(r) \gg \delta V^{\rm struc}(\vec{r})$ is not well satisfied.

Our intention is to correct this defect by the adjustment of E_d, so that we keep the GPT formalism, assuming the hybridization operator fully determined from $\delta V^{\rm vol}(r)$, while the terms appearing in $\delta V^{\rm struc}(\vec{r})$ are explicitly distributed following the GPT.

In Fig. 3 we have reported the k dependence of the radial part of the matrix element $\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle$. We compare it with the corresponding results obtained in the cases of the RMP and pseudoatom GPT.[2] In the present approach the $\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle_{\rm rad}$ are less extended in k space than in the two other approaches, which correspond to more localized d states. The magnitude of $\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle_{\rm rad}$ can be checked if the width of the resonance, W_d, E_d, and the corresponding band-structure potential are known, since we have the relation[6]

$$W_d=4k_d\,|\,\langle \vec{k}_d\,|\,\Delta\,|\,d\,\rangle_{\rm rad}\,|^2 \ , \tag{18}$$

where $k_d=\sqrt{2E_d}$. Using our fitted value for E_d (see the next section), we have compared our W_d estimation with other sources in Table I.

C. Determination of E_d and r_c

In the derivation of the form factor, we must scale E_d relative to the conduction band. This is a source of difficulties. For instance, the pseudoatom approach does not place well E_d relative to the Γ_1 point of the conduction band.[2] In our case we do not expect a good location of Γ_1 since we use the Ashcroft model. This problem is inherent in the good determination of both diagonal and off-diagonal matrix elements of the pseudopotential when using a single-parameter model. This has already been discussed in simple metals, where one finds rather different values of r_c when fitting the off-diagonal matrix element to the L band gap and the diagonal term to the observed equilibrium density, or to the bulk modulus.[28] We have decided to by-pass the previous difficulties by fitting E_d from the total conduction-bandwidth $E_F-\Gamma_1$ given in the literature. As shown by Moriarty,[10] the nonlocality of the simple-metal contribution to the energy difference $E_F-\Gamma_1$ is small and of order 0.01 a.u. in copper, so that our local assumption is not expected to be

TABLE I. Width of the resonance in a.u. (double rydbergs).

		W_d	
This work	GPT[a]	Band-structure calculation[b]	
0.0117	0.0138	0.0142	0.0087

[a] Reference 6.

[b] References 26 and 27.

TABLE II. Volume dependence of the mean d-band energy in a.u.

	Atomic volume	$E_F-\Gamma_1$	E_d
Solid	79.68	0.347	0.157 (0.165[a], 0.127[b])
Liquid	89.54	0.312	0.162 (0.149[a])
Liquid	93.44	0.297	0.157

[a] GPT, Ref. 6.
[b] RMP, Ref. 7.

critical in the present determination of E_d, which is solved from

$$E_F-\Gamma_1=\tfrac{1}{2}k_F^2+\sum_d (\langle \vec{k}_F\,|\,\Delta\,|\,d\,\rangle\langle d\,|\,\vec{k}_F\rangle+\text{c.c.})+\sum_d \frac{\langle \vec{k}_F\,|\,\Delta\,|\,d\,\rangle\langle d\,|\,\Delta\,|\,\vec{k}_F\rangle}{\tfrac{1}{2}k_F^2-E_d}\ , \tag{19}$$

where c.c. is the complex conjugate. The values of $E_F-\Gamma_1$ as a function of lattice spacing have been given by Davis *et al.*[18] We have linearly extrapolated these values to estimate E_d in the liquid state from Eq. (19). Our results are reported in Table II. It is interesting to remark that the value of E_d is almost insensitive to the atomic volume in the investigated range.

There are several ways to obtain r_c from a fitting procedure. We pursue our adjustments on the band-structure data by considering, as Dagens does for the RMP,[7] the $L_2'-\Gamma_1$ difference, which is expressed by

$$\begin{aligned} L_2'-\Gamma_1=\tfrac{1}{2}k_L^2&+\langle \vec{k}_L\,|\,w_A+v_s+w_B\,|\,\vec{k}_L\,\rangle\\ &-\langle -\vec{k}_L\,|\,w_A+v_s+w_B\,|\,\vec{k}_L\,\rangle\\ &-\langle 0\,|\,w_A+v_s+w_2\,|\,0\rangle\ , \end{aligned} \tag{20}$$

which reduces to

$$L_2'-\Gamma_1=\tfrac{1}{2}k_L^2-[w_A(2k_L)+v_s(2k_L)]\ . \tag{21}$$

According to the previous values of E_d, δV^{vol}, and the band-structure value of $L_2'-\Gamma_1$,[18] we find r_c almost insensitive to the change of lattice spacing in the solid between 0 K and room temperature. We obtain $r_c \simeq 1.21$ a.u. and keep this value for the liquid state.

D. Analysis of the form factor

We now turn to the total form factor. Owing to the local simple-metal-limit assumption, the nonlocality entirely comes from the s-d—coupling contribution. In Fig. 4 we have represented the on-Fermi-sphere form-factor values and the corresponding SML result. We compare our results to the first work of Moriarty, where he also used an atomic d-state basis.[6] A slightly different screening function was used by Moriarty, since we employ the Vashista-Singwi local-field exchange-correlation scheme instead of that of Singwi *et al.*[22] However, the difference between the two are unimportant for the form factor. Indeed, the difference between our form factor and Moriarty's is essentially due to our SML representation. The first relevant point revealed by Fig. 4 is that we reasonably reproduce the SML of the GPT from the empty-core-model assumption in place of the full OPW expansion. In fact, in simple metals, for instance, potassium (which has s-p core states similar to those of copper), the empty-core radius is close to the ionic radius.[19] The SML representation of copper is different. Considering the d states to be corelike states leads to a value of r_c which is far from the copper ionic radius, ~1.8 a.u. We also remark that the disappearance of the usual orthogonalization-hole density $n_{\text{OH}}^0(r)$ due to our choice of a local model for the SML is not very drastic, at least for the derivation of the form factor.

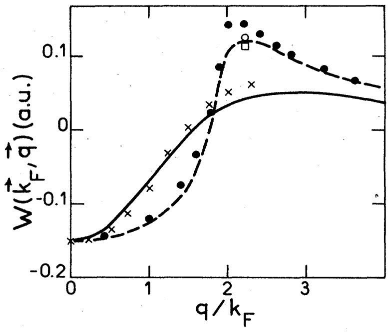

FIG. 4. Form factor of solid copper. Simple-metal limit ($\Delta=0$) of the GPT: present parametrized approach, solid line; Moriarty's *ab initio* approach (Ref. 6), crosses. Total form factor ($\Delta\neq 0$): present parametrized approach, dashed line; Moriarty's *ab initio* approach (Ref. 6), dotted line. The half-band-gap value is indicated by an open square [optical measurements (Ref. 29)] or an open circle [band-structure calculation (Ref. 16)].

The second relevant point concerns the s-d coupling. We obtain a fair agreement with Moriarty's curve, and our solid-state form factor agrees very well with the value 0.0875 a.u. of the half-L band gap measured in copper.[29]

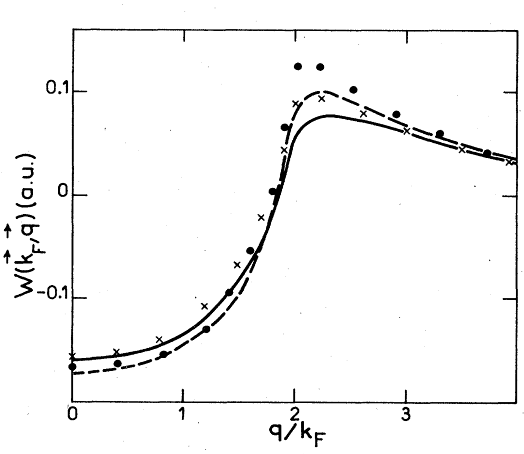

FIG. 5. Volume dependence of the form factor. Solid ($\Omega=79.68$ a.u.): parametrized, dashed line; *ab initio* GPT (Ref. 6), dotted line. Liquid ($\Omega=89.54$ a.u.): parametrized GPT, solid line; *ab initio* GPT (Ref. 31), crosses.

We have considered the volume dependence of the form factor assuming (in agreement with Sec. II C) that E_d and r_c are constant. Therefore, this dependence is included only in the screening charge, δV^{vol}, and the Fermi wave vector appearing in the various integrals. Here, again (Fig. 5), we find that the change of the curves with volume agrees fairly well with the *ab initio* calculations. This increases our confidence in the previous hypothesis concerning r_c and E_d.

III. INTERIONIC INTERACTIONS

In the GPT formalism, the pairwise interionic interactions can be expressed by

$$V(r)=\frac{Z^{*2}}{r}\left[1-\frac{2}{\pi}\int F_N(q)\frac{\sin(qr)}{q}dq\right]+V_{\text{ol}}(r)\ , \tag{22}$$

where $V_{\text{ol}}(r)$ is the overlap potential. $F_N(q)$ is the energy-wave-number characteristic and Z^* is the effective valence. In our case the correction to the chemical valence reduces to the hybridization contribution of Eq. (3) that we obtain,

$$Z^*=Z+\frac{2\Omega}{(2\pi)^3}\int_{k>k_F}\sum_d\frac{\langle\vec{\mathrm{k}}\,|\,\Delta\,|\,d\rangle\langle d\,|\,\Delta\,|\,\vec{\mathrm{k}}\rangle}{(E_k-E_d)^2}d\vec{\mathrm{k}}\ . \tag{23}$$

In the solid, we find $Z^*=1.235$. Thus, in the present case, 0.23 electron per atom is emptied out from the d band through hybridization, while Moriarty obtains 0.4. $F_N(q)$ can be expressed in terms of the previous quantities appearing in the form factor:

$$\begin{aligned}F_N(q)=-\frac{\Omega^2q^2}{4\pi Z^{*2}}\Bigg[&[w_A(q)+v_s(q)]^2\chi(q)+\frac{1}{\pi^3}[w_A(q)+v_s(q)]\left(\int_{k<k_F}d\vec{\mathrm{k}}\frac{w_B(\vec{\mathrm{k}},\vec{\mathrm{q}})}{E_k-E_{k+q}}-\int_{k>k_F}d\vec{\mathrm{k}}\frac{w_R(\vec{\mathrm{k}},\vec{\mathrm{q}})}{E_k-E_{k+q}}\right)\\&+\frac{1}{2\pi^3}\int_{k<k_F}d\vec{\mathrm{k}}\frac{|\,w_B(\vec{\mathrm{k}},\vec{\mathrm{q}})\,|^2}{E_k-E_{k+q}}-\frac{1}{2\pi^3}\int_{k>k_F}d\vec{\mathrm{k}}\frac{2w_B(\vec{\mathrm{k}},\vec{\mathrm{q}})w_R(\vec{\mathrm{k}},\vec{\mathrm{q}})+|\,w_R(\vec{\mathrm{k}},\vec{\mathrm{q}})\,|^2}{E_k-E_{k+q}}\\&-\frac{4\pi}{q^2}\{[1-G(q)]\,|\,n_s(q)\,|^2+G(q)\,|\,n_{\text{OH}}(q)\,|^2\}\Bigg]\ .\end{aligned} \tag{24}$$

Although tedious, the numerical evaluation of (24) is straightforward. We use Animalu's method to obtain the principal-value integrals.[30] A step of $k_F/40$ was found convenient within the standard Simpson method. We find that the upper limit of $4k_F$ is sufficient to ensure good convergence for the s-d—coupling integrals in the range $k>k_F$. An important remark concerns the tentative work that we have done using a semilocal assumption in order to avoid the angular integration in the s-d—coupling integrals. We find in this case very unsatisfactory results when calculating $V(r)$, namely a large overestimation of the repulsive part when compared to the full nonlocal results. Contrary to what happens in the simple-metal case, the presence of the resonant term $w_R(\vec{\mathrm{k}},\vec{\mathrm{q}})$, which is strongly energy dependent, does not allow a simplified local approach for the s-d coupling. Therefore we have no longer pursued this route.

In Fig. 6 we compare the present parametrized GPT $F_N(q)$ with Moriarty's results.[6,31] The differences between the two sets of curves are due to the parametrization and the new formalism employed which we discussed at the beginning of Sec. 2. Before discussing the overlap contribution to $V(r)$, which we intend to fit, it is interesting to present the partial pair potential associated with $F_N(q)$. It corresponds to the simple-metal-limit contribution plus the s-d—coupling effect. It is compared to the equivalent Moriarty potential in Fig. 7. The well-known Friedel oscillations have an amplitude proportional to the form factor at $q=2k_F$.[32] Therefore, the fact that the oscillations are more pronounced in Moriarty's potential is consistent with his larger form factor at $q=2k_F$ (Fig. 4).

The overlap contribution $V^{\text{ol}}(r)$ has been fully investigated in Moriarty's work. In the $V^{\text{ol}}(r)$ expression of Ref. 2, we can distinguish three groups of terms: A first group contains the overlap integrals associated with the orbitals of neighboring sites $\langle d^i\,|\,d^j\rangle$, and the interatomic matrix elements $\langle d^i\,|\,V_{\text{atom}}(\vec{\mathrm{r}}-\vec{\mathrm{R}}_i)\,|\,d^j\rangle$, to which correspond the familiar $dd\sigma$, $dd\pi$, and $dd\delta$ tight-binding matrix elements. The second group includes the s-d—coupling integral over neighboring sites. The third group contains

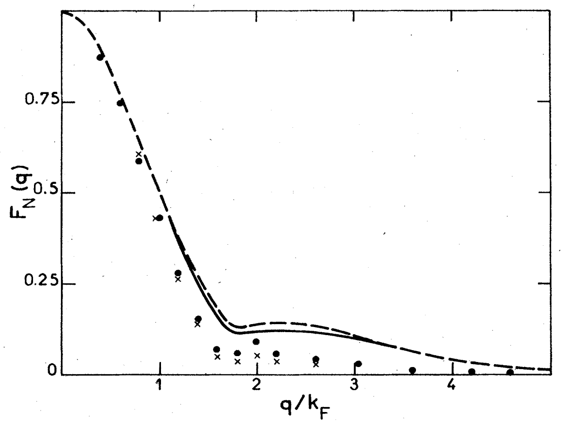

FIG. 6. Normalized energy-wave-number characteristic of solid and liquid copper. The symbols are the same as in Fig. 5.

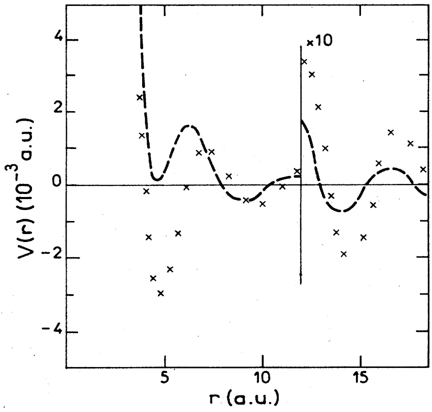

FIG. 7. Interionic interaction without the overlap contribution in solid copper. Parametrized GPT, dashed line; GPT (Ref. 6), crosses.

the core-overlap terms, and its expression depends on the formalism which is employed to describe the core density and the exchange correlation. In the spirit of this work, we do not intend to derive $V^{\mathrm{ol}}(r)$, since the parametrization of the SML has been already done to avoid the inner-core-density calculation, which is needed for the third group of terms in $V^{\mathrm{ol}}(r)$. Moreover, in the evaluation of the second group of terms, the exact expression of $\delta V^{\mathrm{vol}}(\vec{r}-\vec{r}_j)$ is simplified to obtain a tractable derivation of the integrals. A similar problem has been encountered and discussed by Ducastelle[33] in his study of transition metals through the tight-binding approach, where he finally chooses to adjust the overlap potential energy from the bulk properties of the metals. Here we retain the analytic form proposed by Moriarty. It corresponds to an exact GPT calculation with atomic d states, done at the near-neighbor (r_{NN}) and second-neighbor distances in the solid. $V^{\mathrm{ol}}(r)$ reads

$$V^{\mathrm{ol}}(r)=\alpha\left[1+l\left[\frac{r}{r_{\mathrm{NN}}}-1\right]+\beta l^2\left[\frac{r}{r_{\mathrm{NN}}}-1\right]^2\right]\times\exp\left[-\gamma\left[\frac{r}{r_{\mathrm{NN}}}-1\right]\right], \tag{25}$$

where α, β, γ, and l are defined in Ref. 6.

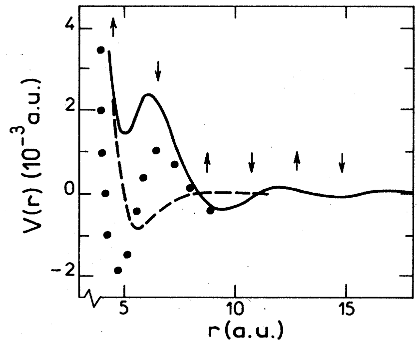

FIG. 8. Interionic interaction in liquid copper at $T=1356$ K and $\Omega=89.54$ a.u. The results correspond to the parametrized GPT with $r_c=1.21$ a.u., $E_d=0.157$ a.u., and $V^{\mathrm{ol}}(r)$ defined by expression (25). SML: dashed line; SML plus s-d coupling, dotted line; SML plus overlap, solid line. The arrows indicate the maximum and minima of the pair-correlation function (Ref. 35).

Expression (25) is not consistent with our derivation of $\delta V^{\mathrm{vol}}(r)$ from relation (10). Nevertheless, it is a good guess for a fit. Moreover, since we want to work with only few parameters, a simple two-parameter form, such as the one used by Gordon,[34]

$$V^{\mathrm{ol}}(r)=A\,e^{-\lambda r}, \tag{26}$$

will also be convenient for our purposes. The adjustment of the parameters A and λ can be done from the data on various interionic-interaction-dependent properties, for instance, the phonon spectra or the elastic constants. Here we use the liquid structure factor and the isothermal compressibility to perform the adjustment. It is first interesting to show how the SML of the pair potential [$\Delta=0$, $V^{\mathrm{ol}}(r)=0$] is modified by the s-d coupling [$\Delta\neq 0$, $V^{\mathrm{ol}}(r)=0$], and by the overlap potential defined by relation (25). We see in Fig. 8 that the s-d coupling modifies the SML result in two ways: First, the repulsive core of the potential is reduced by 10%, and, second, a repulsive barrier is formed at a distance of 6.5 a.u. Adding $V^{\mathrm{ol}}(r)$ restores the repulsive core close to the SML result. However, in using relation (25) we have assumed a solid-density $V^{\mathrm{ol}}(r)$ rather than a liquid-density one, because it is not our purpose here to undertake the lengthy calculation of $V^{\mathrm{ol}}(r)$ for the liquid density, following Moriarty's work.[6] Therefore the influence of $V^{\mathrm{ol}}(r)$ shown in Fig. 8 is only qualitative. In fact, a liquid-density $V^{\mathrm{ol}}(r)$ is presumably less repulsive than the solid-density $V^{\mathrm{ol}}(r)$, and the changes due to $V^{\mathrm{ol}}(r)$ are less marked than those indicated by Fig. 8. In the case of the liquid state we do not expect the differences between the various pair potentials away from the first minimum distance to be very important in the liquid state, since the mean kinetic energy per ion is 6.7 10^{-3} a.u. at the melting point, and is thus largely above the amplitude of the details in the tail of the potential. This remark holds also for Fig. 7. We thus conclude, at this step, that the most influential part of the pair potential is the repulsive core, and that the careful determination of both the s-d coupling and overlap is needed.

IV. LIQUID STRUCTURE AND RELATED PROPERTIES

The link between the interionic interactions and properties such as structure, entropy, constant-volume heat capacity, etc. has proved to be very well realized for liquid metals, by the use of the optimized random-phase approximation, or ORPA. This method of perturbation from the hard-sphere fluid, as a reference system, has been extensively reviewed.[36,15] It has been applied to a variety of liquid metals,[37–39] and to the analysis of the structural trends of these liquid metals.[40] The basic expression that we use for the structure factor is

$$S(q)=\frac{1}{1-[C_\sigma(q)+B(q)-u_A(q)/k_BT]}\,, \tag{27}$$

where $C_\sigma(q)$, $B(q)$, and $u_A(q)$ are, respectively, the Fourier transforms of the direct hard-sphere correlation function $C_\sigma(r)$, the "blip function" associated with the soft-sphere perturbation expansion $B(r)$, and the optimized long-range pair potential $u_A(r)$. Here we inject a cautionary note concerning the use of formula (27), which is an extension of the soft-sphere scheme[41] to the case of potentials with a tail. In the ORPA expansion of Andersen *et al.*,[42] the structure factor is expressed by

$$S(q)=\frac{1}{1-[C_\sigma(q)-u_A(q)/k_BT]}+B(q)\,. \tag{27$'$}$$

However, we have found that (27) agrees better with the result of a Monte Carlo computation than (27').[43] Nevertheless, this is only true for $S(q)$. The price to pay in using (27) instead of (27') lies in the pair-correlation function $g(r)$ obtained from the Fourier transform of (27). Because of the presence of $B(q)$ in the denominator, we cannot obtain an exact zero value for $g(r)$ when r is close to the origin. However, since this defect is spread out by the Fourier transform, it has only a minor influence on $S(q)$. Nevertheless, the success of (27) as well as its limitation in various cases needs further investigation from a more rigorous mathematical analysis.

The choice of the reference hard-sphere system, the optimization method and the technical requirements to compute (27) are exactly the same as those discussed in our previous paper.[15] To estimate the influence of the long-range part of the pair potential, we can consider the results obtained when we neglect the part of the potential for distances beyond the first minimum position r_0. In this case, the soft-sphere structure factor reduces to[15]

$$S_0(q)=\frac{1}{1-[C_\sigma(q)+B(q)]}\,. \tag{28}$$

Once the structure factor is obtained, it is straightforward to calculate the excess entropy per ion by computing

$$\frac{S_E}{k_B}=\frac{S_{ee}}{k_B}+\frac{\partial}{\partial T}\left\{F_\sigma+\frac{2\pi}{\Omega}\int g_\sigma(r)u_A(r)r^2dr+\frac{\Omega T}{4\pi^2}\int\left[1-\frac{S_\sigma}{S_A}+\ln\left[\frac{S_\sigma}{S_A}\right]\right]q^2dq\right\}_{\text{constant }\Omega}\,. \tag{29}$$

S_{ee} is the zero-order free-electron entropy. F_σ is the Carnahan-Starling hard-sphere expression for the free energy.[44] $S_A(q)$ is the structure factor corresponding to (27), but with $B(q)=0$. $g_\sigma(r)$ is the hard-sphere pair-correlation function and $S_\sigma(q)$ is the corresponding structure factor.

The constant-volume heat capacity is obtained from the derivative of S_E versus temperature at constant volume, to which we add the ideal-gas contribution:

$$C_V=T\left[\frac{\partial S_E}{\partial T}\right]_\Omega+\tfrac{3}{2}k_B\,. \tag{30}$$

A further test on the form factor and the liquid structure can be done through the electron-transport properties, and here we shall consider the liquid metal resistivity using the standard Ziman formula:[45]

$$\rho_L=\frac{3}{4}\frac{\pi}{e^2h^3}\frac{\Omega}{k_F^6}\int_0^{2k_F}|w(\vec{k}_F,\vec{q})|^2S(q)q^3dq\,, \tag{31}$$

where $S(q)$ and $w(\vec{k}_F,\vec{q})$ are connected through the determination of the pair potential and the ORPA procedure.

A. The liquid structure

We first consider the influence of the s-d coupling and overlap on the liquid structure by deriving the three structure factors which correspond to the potentials of Fig. 8. These structure factors are presented in Fig. 9 and can

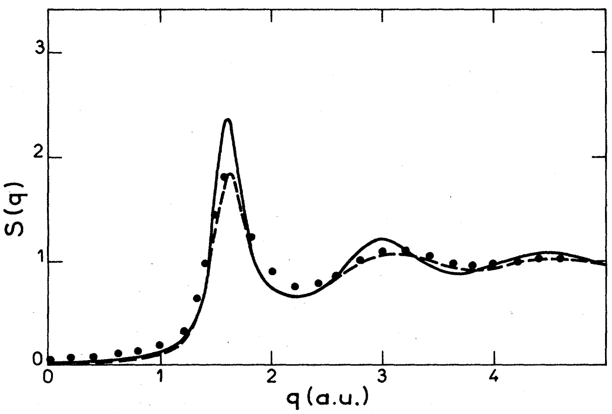

FIG. 9. Contributions of the s-d coupling and overlap to the liquid structure factor of copper at 1356 K. SML, dashed line; SML plus s-d coupling, dotted line; SML plus overlap of relation (25), solid line.

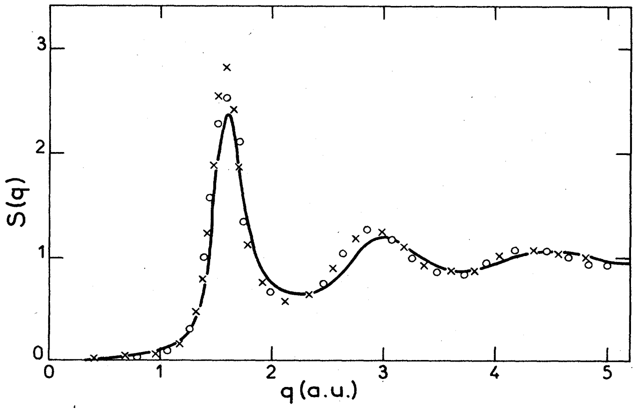

FIG. 10. Structure factors near melting temperature. Theory (ORPA and total pair potential of Fig. 8, $T=1356$ K and $\Omega=89.54$ a.u.), solid line; experiments, neutrons (Ref. 46) (crosses); x rays (Ref. 35) (circles).

TABLE III. Characteristics of the structure factor associated with the various pair potentials. I, simple-metal-limit results; II, SML plus the s-d—coupling influence; III, result II plus the unfitted overlap contribution; IV, result III, but with adjustment of the overlap by $V^{\mathrm{ol}}(r)=A\ e^{-\lambda r}$ ($A=1.43\times10^6$ a.u. and $\lambda=4.55$ a.u.); V, result III, but at a temperature of 1873 K; VI, result IV, but at 1873 K; VII, result III, but assuming the solid-phase pair potential at 0 K and ignoring its change with volume.

	T (K)	$\eta=(\pi/6\Omega)\sigma^3$	$\mu=B(q=\pi/\sigma)/\Omega$	$S_0(0)$	$S(0)$	$S_{\max}$
I	1356	0.507	0.390	0.0171	0.0176 (0.0214[a])	1.82 (2.81[b], 2.55[c])
II	1356	0.388	0.082	0.0482	0.0590 (0.0214[a])	1.83 (2.81[b], 2.55[c])
III	1356	0.467	0.076	0.0246	0.0220 (0.0214[a])	2.35 (2.81[b], 2.55[c])
IV	1356	0.494	0.063	0.0193	0.0212 (0.0214[a])	2.75 (2.81[b], 2.55[c])
V	1873	0.429	0.068	0.0343	0.0315 (0.0283[a])	2.05 (2.40[b], 2.05[c])
VI	1873	0.457	0.056	0.0269	0.0305 (0.0283[a])	2.35 (2.40[b], 2.05[c])
VII	1356	0.469	0.084	0.0241	0.0199 (0.0214[a])	2.33 (2.81[b], 2.55[c])

[a] Experimental data of $S(0)$ deduced from the compressibility (Ref. 47).
[b] Observed maximum value of $S(q)$ from neutron diffraction (Ref. 46).
[c] Observed maximum value of $S(q)$ from x-ray spectrometry (Ref. 35).

also be compared to measurements reported in Fig. 10. In Table III we have reported for each case the value of the hard-sphere packing fraction η of the reference system, the softness parameter μ, the low-q-limit values $S_0(0)$ and $S(0)$, and the maximum value of the structure factor. In the simple-metal-limit approximation (denoted I in Table III), the potential is very soft. This is shown by the value $\mu=0.39$, which is very large indeed. In this case, the "blip-function" expansion is probably not sufficiently accurate, and the results should be certainly improved by using an higher-order expansion. It is clear, anyway, from Figs. 9 and 10, that the SML leads to a very poor description of $S_{\max}$ and $S(q)$ at large wave numbers. On the other hand, the low-q limit of $S(q)$ does not exceedingly deviate from the experimental value reported in Table III. The modification of $S(q)$ due to the s-d coupling is marked at low q since, as indicated in row II of Table III, the low-q limit is about 3 times larger than the value obtained from the compressibility χ_T using the well-known relation $S(0)=k_BT\chi_T/\Omega$. Such a modification at low q comes both from the decrease of the repulsive core diameter (or equivalently η) and the decrease of the softness of the core (or, equivalently, μ). Finally, if we consider the influence of the overlap defined approximately by Eq. (25), we reobtain a curve (Fig. 9) which is in reasonable agreement with the experiment, either at the melting temperature (Fig. 10) or at higher temperature (Fig. 11). There is, in these cases, a fair agreement of the low-q limit of $S(q)$ with the data (row III of Table III). The remaining differences between experiment and theory principally concern the maximum value of $S(q)$ and the shift of the calculated values towards high q (Figs. 10 and 11). We think that such differences do not come from the volume dependence of $V(r)$ since we have found that the liquid structure factor is almost unchanged if it is derived from the pair potential of the solid state, i.e., ignoring any volume dependence in the pseudopotential and in the overlap terms. This is shown by comparing rows III and VII of Table III. Moreover, the results obtained in Sec. II D indicate that both r_c and E_d can be considered to be volume independent, in accordance with the band-structure data. Therefore we attribute most of the remaining differences between theory and experiments in Figs. 10 and 11 to the overlap term. Such differences do not uniquely come from the use of a solid-density $V^{\mathrm{ol}}(r)$ rather than a liquid-density one. Owing to our previous

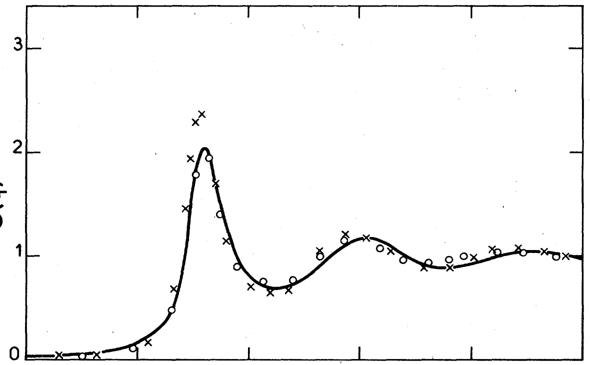

FIG. 11. Structure factor at 1873 K. Theory (ORPA and total pair potential at $\Omega=93.44$ a.u.), solid line; experiments, neutrons (Ref. 46) (crosses); x rays (Ref. 35) (circles).

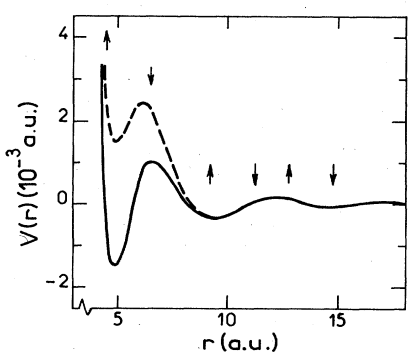

FIG. 12. Influence of the overlap on the pair potential. Result with unfitted overlap, dashed line; result after the fit to the structure factor [$V^{\mathrm{ol}}(r)=1.43\times10^6e^{-4.55}r$], solid line. The arrows indicate the maxima and minima of the pair-correlation function (Ref. 35).

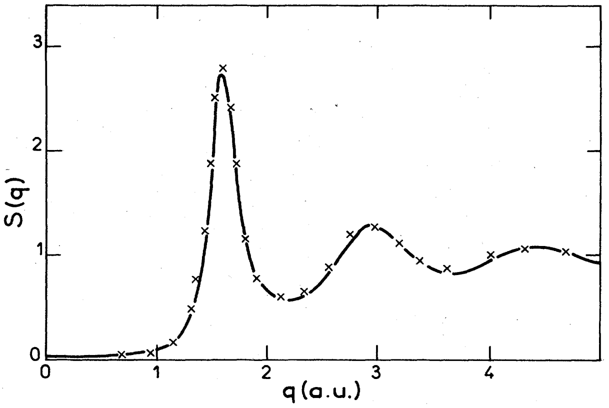

FIG. 13. Structure factor near melting temperature. Parametrized GPT with $v^{\mathrm{ol}}(r)=1.43\times10^{6}e^{-4.55r}$, continuous line; experiment (Ref. 46), crosses.

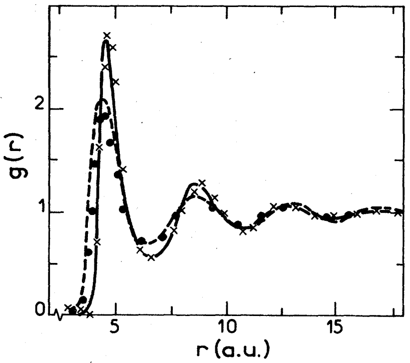

FIG. 15. Pair-correlation function of the liquid near melting temperature: SML (dashed line); SML plus s-d coupling (dotted line); SML plus overlap, $v^{\mathrm{ol}}(r)=1.43\times10^{6}e^{-4.55r}$ (solid line); experiment (Ref. 35), crosses.

comment of Fig. 8, a less repulsive $V^{\mathrm{ol}}(r)$ would also imply a decrease of the softness μ and a corresponding lowering of $S_{\max}$ in row III of Table III, increasing the deviation with the observed structure factor. Following the aim of this work, in which we attempt to define a simple parametrized approach of the GPT, we will fit the overlap term by using the simple expression (26). The two parameters A and λ are adjusted in order to reproduce the experimental value of $S(0)$ and the maximum of $S(q)$.

However, we recall that $S_{\max}$ has no unique determination among the different experiments; for instance, the dispersion is about 10% between x-ray and neutron data;[35,46] therefore we arbitrarily decide to retain parameters which give a close agreement to these last measurements.[46] We find $A=1.43\times10^{6}$ a.u. and $\lambda=4.55$ a.u., and we do not attempt to modify these values with volume since the agreement between the calculated and experimental curves is quite good, both at the melting point where the atomic volume $\Omega=89.54$ a.u. (Fig. 12), and at the temperature of 1873 K where $\Omega=93.44$ a.u. (Fig. 13). We remark that the adjustment of $V^{\mathrm{ol}}(r)$ from the two special points $S(0)$ and $S_{\max}$ also improves the agreement of the curves at high-q values. The change of the pair potential due to the fit of the $V^{\mathrm{ol}}(r)$ part is illustrated in Fig. 14. We note that the two curves are qualitatively the same, but that the overlap is appreciably reduced in the vicinity of the most probable distance, $r_{\mathrm{NN}}=4.72$ a.u., in the liquid. On the other hand, the fitted overlap potential is found to be harsher than the unfitted one, since we find a smaller value of μ (rows III and IV of Table III). Moriarty has also discussed similar changes by comparing the overlap potential of Zn using the standard and optimized GPT.[10]

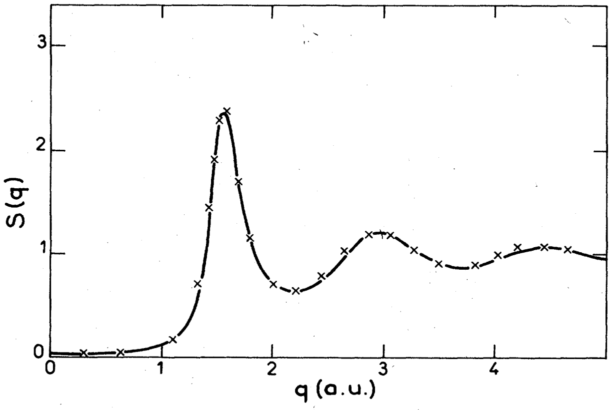

FIG. 14. Structure factor at 1873 K. Parametrized GPT with $v^{\mathrm{ol}}(r)=1.43\times10^{6}e^{-4.55r}$, continuous line; experiment (Ref. 46), crosses.

Finally, to conclude our discussion of the influence of the s-d coupling and overlap on the liquid structure, we have calculated the pair-correlation functions. It is clear from Fig. 15 that the effect of the overlap is important at short range since the most probable distance in the liquid changes from 4.35 to 4.60 a.u., in agreement with the data of Ref. 35. Moreover, we note that the overlap and s-d—coupling components both emphasize the correlation between the minima and maxima of $V(r)$ and the corresponding maxima and minima of $g(r)$ (Fig. 14). One could imagine that an *ad hoc* simple-metal pair potential would be able to reproduce a $g(r)$ value in agreement with the data, but such an artificial procedure would certainly fail for other properties, such as the observed band gap.

B. Excess entropy and heat capacity

We report the calculated values of S_E and C_V in Table IV. We note the importance of the contribution of the overlap to the excess entropy. The good agreement with the experimental data in row IV confirms our previous fit to the liquid structure factor. On the other hand, we find that the heat capacity seems to be essentially determined by the simple-metal contribution (row I). The discrepancy between the results in rows III and IV using two different overlaps is not contradictory, but indicates that the differences between experiment and theory comes, at first, from the difficulties in the overlap estimation. Nevertheless, the results in rows IV and VI can be considered to be rather successful, since to calculate C_V we must deal with

TABLE IV. Excess entropy and constant-volume heat capacity per ion. k_B is the Boltzmann constant. The labels I,II, . . . , VII have the same meaning as in Table III.

	$-S_E/k_B$	C_V/k_B
I	2.11	2.96
II	2.08	3.11
III	3.07	2.39
IV	3.69 (3.60[a])	3.25 (2.45[c], 3.0[d])
V	2.51	3.21
VI	3.04 (3.12[b])	2.66
VII	3.02	2.46

[a] Experimental value of the excess entropy quoted in Ref. 48.

[b] The value of S_E at 1873 K is obtained after integrating the well-known relationship $C_V dT = T\,dS$ between 1356 and 1873 K, assuming $C_V \approx 3k_B$.

[c] Experimental values of C_V from Ref. 49.

[d] Experimental values of C_V from Ref. 50.

the second derivative of the free energy at constant volume.

C. Liquid resistivity

We have calculated the resistivity with and without the soft-sphere approximation for the structure factor. It is clear from Table V that the oscillatory part of $V(r)$ has only a very small influence on the liquid resistivity. On the other hand, using the solid-state form factor in place of the liquid one is a poor approximation, since the resistivity is overestimated by nearly a factor of 2 (rows III and VII of Table V). We thus agree with Moriarty's comments concerning the necessary calculation of the pseudopotential at the liquid density.[6] With the SML we completely fail in explaining the observed value of the resistivity (row I), and it is clear that both the *s-d* coupling, which drastically modifies the form factor, and the overlap interactions, are the important ingredients which determine the electronic-transport mechanism (rows II and IV). The comparison between rows III and IV once more indicates that the fitting of $V^{\mathrm{ol}}(r)$ to the structure factor is attractive. Moreover, since $V^{\mathrm{ol}}(r)$ is not involved in the form factor itself, the good agreement with experiment obtained for both the resistivity and its temperature dependence again justifies the parametrization of the form factor by r_d and E_d.

V. CONCLUSION

In this work we have considered the generalized pseudopotential theory in the case of the noble metals. We have built a parametrized approach from the terms which correspond to the simple-metal limit, *s-d* coupling, and overlap contribution in the GPT formalism. To fit the first two contributions, we have used the band-structure data. We have shown that the overlap potential can be adjusted by considering its effect on the liquid structure.

We find that the empty-core potential is adequate to mimic the SML if the core radius r_c is suitably adjusted. This indicates, to a good extent, that the details of the interactions between the free-electron-like particles and the ions can be ignored in noble metals. Such an observation, which takes place here in the framework of the GPT, has a more general meaning in view of the similar results obtained by Dagens and Wills and Harrison in their different approaches.

We have calculated the *s-d*—coupling terms, following the GPT exactly using a development on the basis of atomic *d* states. By considering the contribution of the *s-d* coupling to the total width of the conduction band, we have adjusted the mean energy E_d of the *d* band.

From the previous parametrization of the SML and the *s-d* coupling, we obtain the width of the resonance and the *L* band gap close to those of other calculations and optical measurements. Moreover, the form factors that we obtain, either in the solid state or in the liquid state, are in overall agreement with those of the corresponding *ab initio* approach.

Using the ORPA we have determined the influence of the overlap on the liquid structure of copper. We find that the exact overlap form proposed by Moriarty is already a good estimation which needs only a smooth adjustment. We have proposed a two-parameter overlap potential to investigate the sensitivity of the liquid properties to the parameters. We find that the parameters r_c, E_d, and those of the overlap are almost insensitive to volume changes in solid and liquid under normal pressure. We have analyzed the deviations from the SML approxima-

TABLE V. Resistivity of liquid copper. The values ρ_0 and ρ correspond, respectively, to the $S_0(q)$ and $S(q)$ structure factors. The labels I,II, . . . , VII have the same meaning as in Table III.

	ρ_0 ($\mu\Omega$ cm)	ρ ($\mu\Omega$ cm)	$\frac{T}{\rho_0}\left[\frac{\partial \rho_0}{\partial T}\right]_\Omega$	$\frac{T}{\rho}\left[\frac{\partial \rho}{\partial T}\right]_\Omega$
I	2.77	2.70	1.09	1.12
II	41.36	39.82	0.35	0.39
III	27.53	27.19	0.37	0.39
IV	23.46	22.33 (21.0[a])	0.36	0.41 (0.4[a])
V	32.66	32.62	0.34	0.35
VI	28.04	27.21	0.33	0.36
VII	49.27	48.72	0.25	0.29

[a] Experimental value quoted in Ref. 48.

tion when the *s-d* coupling and overlap are taken into account. We find that the SML gives a poor description of properties such as liquid structure, entropy, and resistivity, while a fair agreement with experiment is obtained when *s-d* coupling and overlap are included. Our analysis points out the influence of the *d* electrons on the structure as a delicate balance between the two previous contributions.

We finally conclude that the development of the GPT from the basis of the atomic *d* states can be conveniently parametrized without losing too much of the specificity of the approach, i.e., the separation into simple-metal, *s-d*—coupling, and overlap terms. In our work we entirely avoid the intricate calculation of the overlap, and therefore our point of view cannot replace any first-principles determinations. For instance, we have by-passed the problem of the unfilling of the *d* states through the parametrization. Moriarty has clearly indicated that the next theoretical improvements would follow the line of the partially filled-*d*-band scheme. However, the present parametrized approach could be useful as a first step in the cases which are not easily tractable in a detailed theory, such as, for instance, in the investigation of the specific effects of the *d* electrons on the alloys or on the surface properties of noble metals.

APPENDIX

In Sec. II B we noted that the extra potential curves $\delta V^{\rm vol}(r)-\delta V(0)$ are close to a parabolic form. Very little error is made by using the expansion $r^2/2r_{\rm WS}^3+br+c$ instead of the exact result, once the coefficients b and c have been conveniently adjusted. In this case, the *s-d*—coupling matrix elements are easier to handle and are expressed by

$$\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle = -4\pi\Omega^{-1/2}Y_{2m}(\vec{k})\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle_{\rm rad}\,, \tag{A1}$$

where the $Y_{2m}(\vec{k})$ are the spherical-harmonic functions and the radial part reads

$$\begin{aligned}\langle \vec{k}\,|\,\Delta\,|\,d\,\rangle_{\rm rad} = \frac{1}{2r_{\rm WS}^3}(\langle \vec{k}\,|\,r^2\,|\,d\,\rangle_{\rm rad} & \\ -\langle \vec{k}\,|\,d\,\rangle_{\rm rad}\langle d\,|\,r^2\,|\,d\,\rangle_{\rm rad}) & \\ +b(\langle \vec{k}\,|\,r\,|\,d\,\rangle_{\rm rad}-\langle \vec{k}\,|\,d\,\rangle_{\rm rad}\langle d\,|\,r\,|\,d\,\rangle_{\rm rad}) &\end{aligned} \tag{A2}$$

The radial part of the *d* atomic wave functions are expressed in the form[24]

$$R_{32}(r) = \sum_{i=1}^{5} C_i N_i r^2 e^{-\xi_i r}\,, \tag{A3}$$

where ξ_i and C_i are the coefficients of the basis of the $4s^1 3d^{10}$ configuration, and $N_i=[6!]^{1/2}[2\xi_i]^{7/2}$. In this case, the terms of (A2) can be expressed in algebraic form:

$$\begin{aligned}\langle \vec{k}\,|\,d\,\rangle_{\rm rad} &= 48\sum_{i=1}^{5} C_i N_i \xi_i \frac{k^2}{(\xi_i^2+k^2)^4}\,,\\ \langle \vec{k}\,|\,r\,|\,d\,\rangle_{\rm rad} &= 48\sum_{i=1}^{5} C_i N_i k^2 \frac{7\xi_i^2-k^2}{(\xi_i^2+k^2)^5}\,,\\ \langle \vec{k}\,|\,r^2\,|\,d\,\rangle_{\rm rad} &= 384\sum_{i=1}^{5} C_i N_i \xi_i k^2 \frac{7\xi_i^2-3k^2}{(\xi_i^2+k^2)^6}\,,\\ \langle d\,|\,r\,|\,d\,\rangle_{\rm rad} &= 7!\sum_i\sum_j C_i C_j N_i N_j/(\xi_i+\xi_j)^8\,,\\ \langle d\,|\,r^2\,|\,d\,\rangle_{\rm rad} &= 8!\sum_i\sum_j C_i C_j N_i N_j/(\xi_i+\xi_j)^9\,.\end{aligned} \tag{A4}$$

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