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## FORMULATIONS FOR THE TREATMENT OF MULTI-BAND NON-SIMPLE LIQUID METALS. APPLICATION TO THE WILSON TYPE METAL-NON METAL TRANSITION

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**Résumé.** — On développe une méthode qui permet d'évaluer les propriétés électroniques des métaux liquides et amorphes, des alliages et des semiconducteurs liquides. Cette méthode est particulièrement adéquate pour traiter les métaux de transition, les métaux nobles et les terres rares. On présente des expressions explicites pour la fonction de Green à un électron dans l'approximation à un site *selfconsistente*. Les difficultés inhérentes aux systèmes présentant des dégénérescences orbitales, une probabilité de *hopping* dépendant des angles et de l'hybridation sont grandement simplifiées dans notre formalisme. La méthode est appliquée au calcul de la densité d'états pour un système présentant une transition métal-isolant du type Wilson.

**Abstract.** — Methods are developed for evaluating the electronic properties of non-simple liquid and amorphous metals, their alloys and liquid semi-conductors. By non simple metals we mean those for which the nearly free electron model does not hold, such as transition, noble and rare earth metals. Explicit expressions for the one electron Green's function of such systems are evaluated within the self consistent single site framework. The formalism presented effects considerable simplification of technical difficulties inherent in the treatment of orbital degeneracy, angular dependent hopping and hybridization. An application of these methods to the calculation of the density of states for a system undergoing a Wilson-type metal-non metal transition is presented in the form of numerical calculations on expanded liquid mercury. The results are also compared with various calculations on expanded crystalline mercury. The dependency of the critical density on various model parameters, type of pair distribution, as well as different types of wave functions is analyzed.

1. **Introduction.** — Calculation of the electronic density of states in liquid metals presents formidable problems. One approach is to presume that the crystalline band structure resembles that of the liquid state [1] and perform calculations on crystals of appropriate density. Another method is to calculate results for finite clusters which are made to simulate very large systems [2]. One may, on the other hand attempt to deal with an infinite system by making simplifying approximations for the correlation functions describing the structural disorder. The latter approach involves averaging the Green's functions  $\langle G \rangle$  over the appropriate atomic configurations. Most such methods have concentrated on treating the mean effect of  $N - 1$  atoms on an arbitrarily chosen  $N$ th atom as a kind of self consistent effective medium (the so-called self consistent single site approximation-SSSA [3-7]). These approximations include the coherent potential approximation (CPA) [8-10] and various related simplifications [11, 5]. Within such approximations the averaged single particle Green's function

$\langle G \rangle$  is related to the mean density of states, conductivity and Hall coefficient.

Some of the above SSSA work has included numerical results for the density of states within a tight binding approximation, but these have all been restricted to one band cases. For non simple liquid metals, a multi band treatment which deals with orbital degeneracy, angular dependent hopping and hybridization is indispensable. A straightforward extension of SSSA formalisms to multi-band cases results in matrix equations of considerable formal difficulties. In this paper we outline a formalism in which these difficulties are avoided.

As an application of this formalism we shall present the results of a number of numerical calculations of the density of states of expanded liquid Hg. Any divalent metal, whether crystalline or liquid, can be expected to transform to an insulating state at a sufficiently low density. In both cases the transition can be understood from the single particle point of view as resulting simply from the narrowing and

separation of valence and conduction bands which overlap at normal densities. In the low density limit these correspond to highest occupied and lowest unoccupied atomic levels, regardless of the presence of long range order. Liquid Hg has been an especially attractive object of experimental study because of its relatively accessible critical point [12-16]. The appearance of an optical gap at a density between 5 and 6 g cm<sup>-3</sup> [16] can be associated with the above mentioned band separation. One may interpret the semi-conducting behaviour observed up to about 9 g cm<sup>-3</sup> as resulting from disorder induced localization [17]. We take this point of view in what follows, although it may be at variance with recent Knight shift measurements [18]. Thus we shall calculate values for an optical critical density,  $n_c$ , at which a band gap appears, and examine its dependency on various model parameters, pair distributions and different types of wave functions. Finally we compare our results with those of calculations on expanded crystalline Hg, in an attempt to examine the role of disorder in determining  $n_c$ .

2. **Formalism.** — We illustrate the formalism with a tight binding Hamiltonian :

$$\mathcal{H} = \sum_{i,v} E_{i,v} a_{i,v}^+ a_{i,v} + \sum_{i \neq j} \sum_{\mu} \sum_{\nu} t_{ij}^{\mu\nu} a_{i,\mu}^+ a_{j,\nu} \quad (1)$$

where  $a_{i,v}^+$  ( $a_{i,v}$ ) designates the creation (annihilation) operator for an electron in the orbital  $\varphi_v(\mathbf{r} - \mathbf{R}_i)$ , and atomic basis function appropriate to the  $\nu$ th band, centered at the  $i$ th site : The summations over  $i$  and  $j$  are taken over a given configuration of disordered atomic sites.

In what follows, we assume the atomic level,  $E_{i,v}$ , to be site independent, and the usual transfer energy,  $t_{ij}^{\mu\nu}$ , to be a function of  $\mathbf{R}_i - \mathbf{R}_j = \mathbf{R}_{ij}$ . It is defined as

$$t_{ij}^{\mu\nu} = t^{\mu\nu}(\mathbf{R}_{ij}) = \int \varphi_{\mu}^*(\mathbf{r} - \mathbf{R}_{ij}) v(|\mathbf{r} - \mathbf{R}_{ij}|) \varphi_{\nu}(\mathbf{r}) d^3r.$$

Note that  $v(|\mathbf{r} - \mathbf{R}_{ij}|)$  is a spherical atomic potential.

A one-electron Green's function for a given configuration of atoms is defined by

$$G_{ij}^{\mu\nu}(E) = \left\langle 0 \left| a_{i,\mu} \frac{1}{E^+ - \mathcal{H}} a_{j,\nu}^+ \right| 0 \right\rangle. \quad (2)$$

The averaged Green's function is usually obtained by expanding the right-hand side of this equation in terms of an unperturbed locator  $G^{(0)} = (E^+ - E_v)^{-1}$  and the transfer energy  $t_{ij}^{\mu\nu}$ , and then taking the average of each expanded term and resumming the averaged terms. If we make the assumption of zero overlap between atomic functions on different sites, we may define the mean density of states as [19]  $D(E) = -\pi^{-1} \text{Im Tr} \langle \mathbf{G}_{ii} \rangle$ , where a Green's function matrix  $\langle \mathbf{G}_{ii} \rangle$  is defined such that its  $\mu\nu$ th matrix element is  $\langle G_{ii}^{\mu\nu} \rangle$ . We have assumed statistical homogeneity, and thus made  $\langle G_{ii}^{\mu\nu} \rangle$

site independent. The restriction of zero overlap between atomic functions on different sites can always be removed and the corresponding self-consistent equations obtained. The proof to follow is also easily generalized to the cases where nonorthogonality effects and some higher-order diagonal terms are taken into account [19].

In all SSSA theories, the Green's function is determined by a selfconsistency equation of the form  $\langle \mathbf{G}_{ii} \rangle = \int \mathcal{F}(\mathbf{k}) d^3k$ , where  $\mathcal{F}(\mathbf{k})$  is a functional matrix of  $\langle \mathbf{G}_{ii} \rangle$  and  $V(\mathbf{k})$ . The  $\mu\nu$ th matrix element of  $\mathbf{V}(\mathbf{k})$  is defined by

$$v^{\mu\nu}(\mathbf{k}) = \int t^{\mu\nu}(\mathbf{R}) g(R) \exp(i\mathbf{k} \cdot \mathbf{R}) d^3R,$$

in which  $g(R)$  is a pair distribution function. Therefore, the solution  $\langle \mathbf{G}_{ii} \rangle$  must be determined by an iterative procedure. As a practical matter, solving the above three dimensional integral numerically with reasonable accuracy is somewhat difficult.

Because the iterative nature of the solution requires that it be solved repeatedly, the problem becomes extraordinarily cumbersome. Although the angular part of the integration is trivially done analytically in the case of s bands, this is not in general the case for non spherical atomic wave functions. In addition to this, the more bands that are taken into account, the more matrix elements defining  $\langle \mathbf{G}_{ii} \rangle$  must be determined in a simultaneously self consistent manner. The angular integrations may be performed analytically, however, as follows : If we assume spherically symmetric atomic potentials, we may take our basis (either in the case of muffin tin potentials or tight binding) to depend on the usual principal, angular and magnetic quantum numbers,  $n, l, m$ .

Then it can be shown (see reference [20] for details) that the matrix elements for the averaged Green's function may be written

$$\begin{aligned} \langle G_{ii}^{\mu\nu} \rangle &\equiv \langle G_{nlm,n'l'm'} \rangle = \\ &= \int \mathcal{F}_{nlm,n'l'm'}(\mathbf{k}) d^3k / (2\pi)^3 \end{aligned} \quad (3)$$

and we may separate out the angular and radial parts of the integral in the following form

$$\begin{aligned} \langle \mathbf{G}_{ii} \rangle &= \mathbf{G}^{(0)} + \mathbf{G}^{(0)} \int \mathbf{T}_{\varphi}(\varphi_k) \mathbf{T}(\theta_k) \mathbf{F}(k) \\ &\quad \times \mathbf{T}^t(\theta_k) \mathbf{T}(\varphi_k) \frac{d^3k}{(2\pi)^3} \langle \mathbf{G}_{ii} \rangle \end{aligned} \quad (4)$$

where the  $k$  vector,  $k = (k, \theta_k, \varphi_k)$ , the  $\mathbf{T}$  matrices are rotation matrices and functions of angle alone, and  $\mathbf{F}(k)$  is a function only of the magnitude,  $k$ . Using eq. (4) we may perform the angular integrations analytically, and we find

$$\langle \mathbf{G}_{ii} \rangle = \mathbf{G}^{(0)} + \mathbf{G}^{(0)} \Sigma \langle \mathbf{G}_{ii} \rangle \quad (5)$$

where the matrix elements of  $\Sigma$  are given by

$$\Sigma_{nlm,n'l'm'} = \frac{1}{2l+1} \delta_{ll'} \delta_{|m||m'|} \times \\ \times \sum_{m_1} F_{nl|m_1|n'l|m_1|}(k) \frac{4\pi k^2 dk}{(2\pi)^3}. \quad (6)$$

In the case of the SSSA scheme of reference [5], taken as an example, we find the matrix  $\mathbf{F}$  given by

$$\mathbf{F}(k) = \{ \mathbf{u}(k) [\mathbf{1} - \rho \langle \mathbf{G}_{ii} \rangle \mathbf{u}(k)]^{-1} + [\mathbf{u}_0(k) - \\ - \mathbf{u}(k)] \rho \langle \mathbf{G}_{ii} \rangle, \mathbf{u}(k) \}. \quad (7)$$

The matrix elements of  $\mathbf{u}$  in eq. (7) are

$$u(k)_{nlm,n'l'm'} = \\ = 2\pi \delta_{|m||m'|} \sum_{N=|l'-l|}^{l'+l} \sum_{M=-\min(l,l')}^{\min(l,l')} i^{N(2N+1)(-1)^{M-|m|}} \\ \times \langle l'NM0 | l'NlM \rangle \langle l'NM0 | l'Nlm \rangle \\ \times \frac{2}{2l+1} \int_{nl|M|,n'l'|M|} J_N(kR) U(R) g(R) R^2 dR \quad (8)$$

where the  $\langle l'NM0 | l'NlM \rangle$  are Clebsch-Gordon coefficients, and  $U(R)$  is the transfer energy integral, a function only of the separation between centers,  $R$ . Eq. (8) illustrates the simplification of the remaining matrix problem, which is blocked into considerably more tractable submatrices.

**3. Numerical results.** — Eq. (4) (8) have been applied to liquid Hg with a number of different sets of approximations. The crudest calculation chose simple Slater 2S and 2P wave functions as a basis. The pair distribution function  $g(R)$  of eq. (8) was that of a simplified hard core liquid ( $G(R)$  equal to 0 or 1 accordingly as  $R < \sigma$  or  $\geq \sigma$ ) where  $\sigma$  was first taken to be determined on the basis of Ashcroft-Leckner theory for normal densities. Because of the large value ( $\sigma = 5.4$  a. u.) compared to the extent of the nodes of the actual 6S and 6P functions of Hg, the simple Slater functions are not totally unreasonable if the effective Bohr radius is chosen to match the charge density maximum of the Hermann-Skillman [21] Hg wave functions. The large hard core plus the relatively low densities of interest make our further assumption of orthogonality quite reasonable: at the distance of closest approach the S-S overlap was 0.035 in this approximation. Calculating the density of states at various densities results in a gap opening at about  $2 \text{ g cm}^{-3}$ .

Some obvious questions arising are the extent to which this result depends on *a*) details of wave functions, *b*) form of  $g(R)$ , *c*) size of  $\sigma$ , and in general, *d*) liquid disorder. The results of further calculations presented below are meant to be some first steps towards providing answers to these questions.

*a*) We have found that although the general shape (band widths, curvatures etc.) of the density of states at  $n_c$  is not especially sensitive to choice of wave functions, the value of the density itself is very sensitive to this choice. We repeated the above calculation using Hg 6S and 6P functions from a non relativistic Hermann-Skillman calculation [22], and the resulting self consistent Hartree-Fock-Slater potential in the transfer energy integral. This results in an  $n_c$  of about  $3 \text{ g cm}^{-3}$ . A plot of the density of states resulting from these wave functions at a density somewhat below  $n_c$  is shown in figure 1. It is typical of all our

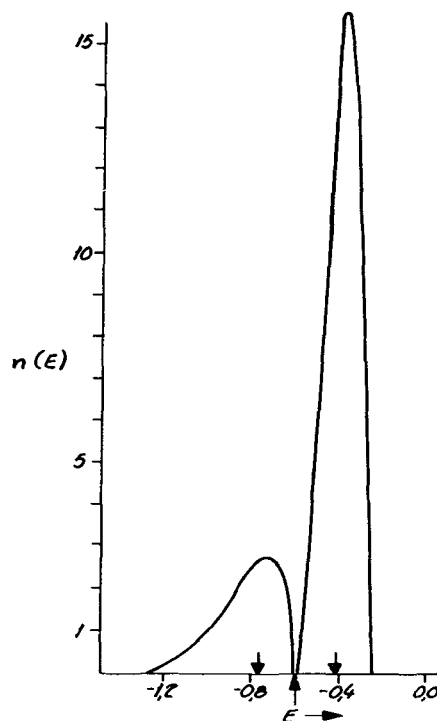


FIG. 1. — Density of states of Hg at a density just below  $n_c$ . Energy in Rydbergs. Inverted arrows ( $\downarrow$ ) mark the energies of the atomic levels ( $E_{i,v}$  of eq. (1)) and an upright arrow ( $\uparrow$ ) denotes the Fermi energy.

calculations. The use of relativistic Hermann-Skillman functions and potentials, keeping all other parameters as above, results in an  $n_c$  of about  $4 \text{ g cm}^{-3}$ . This sensitivity of the exact value of  $n_c$  to choice of wave functions and potentials has its counterpart in crystalline calculations, as we indicate below.

*b*) In contrast to point *a*) we have found that improvement of the pair distribution function by using the results of a Percus-Yevic equation, in the case of any given wave function, does not result in equally significant changes in  $n_c$ , so long as the hard core diameter  $\sigma$  is left unchanged.

*c*) Variation of  $\sigma$  in the above calculations, however, results in a very strong variation in  $n_c$ . Results for  $n_c$  over a wide variation in  $\sigma$  for simplified wave functions and pair correlation are shown in figure 2. The simpli-

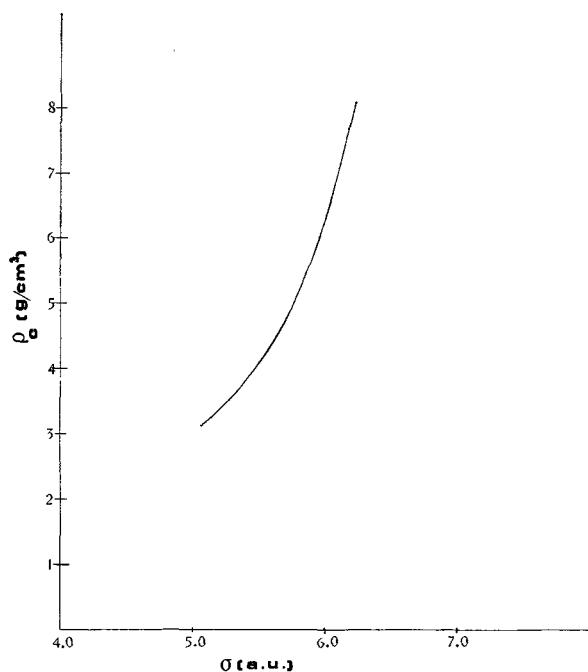


FIG. 2. — Density at which the bands separate,  $n_c$ , as a function of hard core diameter,  $\sigma$ .

fied wave functions were chosen as Slater functions whose orbital exponents were chosen to give the same  $n_c$  at  $\sigma = 5.4$  a. u. (Ashcroft-Leckner theory) as relativistic Hermann-Skillman functions. These simplifications were made to cut down on the extensive computer time required for a smooth curve. Similar variations in the case of the actual Hermann-Skillman functions were found.

d) A number of calculations of  $n_c$  for expanded crystalline Hg have been performed. A simple local pseudopotential calculation in a few symmetry points of the Brillouin zone [23] results in a gap opening at about  $8.5 \text{ g cm}^{-3}$ . This density was found to be approximately independent of crystal structure. A more sophisticated pseudopotential calculation [24] eliminates this structural independence and gives different values for the critical density in FCC, BCC and SC structures ( $6.5$ ,  $5.5$ , and  $4.0 \text{ g cm}^{-3}$  respectively). These latter results are roughly equivalent to those obtained with a relativistic KKR method [25] except that the transition densities are somewhat higher ( $5.5 \text{ g cm}^{-3}$  for SC and  $8.2 \text{ g cm}^{-3}$  for FCC). Other KKR calculations (26) indicate sensitivity of  $n_c$  to details of the muffin tin potential, corresponding to points a) and c) above. Two generally expected effects of the liquid state as compared to the crystalline are observed. The lower occupied band in the liquid is in general more than twice as broad as in the crystal, and, as a result of the tailing of both bands the gap opens up in the liquid at lower densities.

All the above calculations indicates ensitivity of  $n_c$  to details of electronic structure. Among other things one clearly may no longer choose to ignore hybridization effects. Furthermore the extreme sensitivity to  $\sigma$  suggests the possibility of the importance of temperature effects. Thus it is doubtful whether detailed agreement between experiment and theory will result from simple models, and we must conclude that unambiguous theoretical description of the observed data must await either further elaboration of the available models, or new ones.

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