out, however, that the shifts predicted from Eq. (1) for the higher states spoil the agreement[1] between the observed $n=2,3,4,\infty$ lines and isotropic binding energies. A consistent quantitative description of the exciton series of $\mathrm{PbI}_2$ can only be given by taking account of both the anisotropy and the layer orthogonality repulsion. We hope soon to be able to present a detailed calculation with ellipsoidal wave functions.

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# Tight-Binding Model of Electronic States in a Liquid Metal

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As a model of an amorphous system we consider a collection of atoms with one atomic orbital per site, in terms of which the one-electron Green's function is expanded. We apply multiple-scattering techniques to this system, and obtain the quasicrystalline approximation of Lax and the self-consistent approximation of Schwartz and Ehrenreich. Results are given for the electronic density of states using pair distribution functions for random and hard-sphere liquids.

Tight-binding representations have recently been found to give good results[1] for electronic states in systems for which the wave functions are actually somewhat extended, provided that the Bloch sum is carried out for many neighbors and nonorthogonality is taken into account. It therefore appears worthwhile to apply tight-binding methods to amorphous systems.

As an initial step in this direction, we consider a collection of atoms in some distribution and assume that the wave function can be expanded in terms of one atomic state per atom. The result is a simple model for liquid metals. We have applied multiple-scattering techniques to this problem, and report here results corresponding to the quasicrystalline approximation (QCA) of Lax[2] and the self-consistent approximation (SCA) of Schwartz and Ehrenreich.[3,4] The relationship to the substitutional alloy problem will be shown, and in particular to the coherent potential approximation (CPA) of Soven[5] and Velicky and Ehrenreich.[6] Our results are more general than the work of Beeby and Edwards,[7] and our averaging method is better defined than that of Takeno.[8]

We work with the one-electron Green's function $\mathcal{G}_t(\vec{r},\vec{r}\,')$ which obeys the equation

$$(\omega-\mathcal{H})\mathcal{G}_t(\vec{r},\vec{r}\,')=\delta(\vec{r}-\vec{r}\,'), \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian operator for the system of an electron in some configuration of atoms. We assume an expansion of $\mathcal{G}_t$ in terms of atomic orbitals $\varphi_j(\vec{r})=\varphi(\vec{r}-\vec{R}_j)$,

$$\mathcal{G}_t(\vec{r},\vec{r}\,')=\textstyle\sum_{ij}\varphi(\vec{r})\mathcal{G}_{ij}\,\varphi_j(\vec{r}\,'), \tag{2}$$

and find that $\mathcal{G}_{ij}$ obeys the equation

$$\textstyle\sum_l(\omega\mathcal{S}_{il}-\mathcal{H}_{il})\mathcal{G}_{lj}=\delta_{ij}, \tag{3}$$

where

$$\mathcal{S}_{il}=\int\varphi_i(\vec{r})\varphi_j(\vec{r})\,d^3r, \tag{4}$$

$$\mathcal{H}_{il}=\int\varphi_i(\vec{r})\mathcal{H}\varphi_j(\vec{r})\,d^3r, \tag{5}$$

are overlap and Hamiltonian matrices, respectively. We shall not assume orthogonal orbitals, but we can lump $\mathcal{S}_{il}$ in with $\mathcal{H}_{il}$ for $i\neq l$ by writing $\mathcal{H}_{il}'=\mathcal{H}_{il}-\omega\mathcal{S}_{il}$. We then expand $\mathcal{G}$ in powers of $\mathcal{H}_{ij}$:

$$\mathcal{G}_{ij}=\frac{\delta_{ij}}{\omega-\mathcal{H}_{ii}}+\frac{(1-\delta_{ij})\mathcal{H}_{ij}'}{(\omega-\mathcal{H}_{ii})(\omega-\mathcal{H}_{jj})}+\sum_l\frac{\mathcal{H}_{il}'\mathcal{H}_{lj}'}{(\omega-\mathcal{H}_{ii})(\omega-\mathcal{H}_{ll})(\omega-\mathcal{H}_{jj})}+\cdots. \tag{6}$$

Since we shall be averaging over atomic positions, it is convenient to work with a continuum Green's function

$$\mathcal{G}(\vec{r},\vec{r}\,')=\textstyle\sum_{ij}\delta(\vec{r}-\vec{R}_i)\mathcal{G}_{ij}\delta(\vec{r}\,'-\vec{R}_j), \tag{7}$$

in which $\vec{R}_i$ is essentially fixed at $\vec{r}$, and $\vec{R}_j$ at $\vec{r}\,'$. We now make several simplifying assumptions: (1) $\mathcal{H}_{ii}=H_0$ is a constant independent of the distribution of neighbors; and (2) $\mathcal{H}_{ij}$, $j\neq i$, is a function only of the relative positions, $H(\vec{R}_i-\vec{R}_j)$. Clearly the latter applied also to $\mathcal{H}_{ij}'$. Equation (6) can now be rewritten as

$$\begin{aligned}\mathcal{G}(\vec{r},\vec{r}\,')=\sum_i\tau_i(\vec{r})\delta(\vec{r}-\vec{r}\,')+\sum_{i\neq j}\tau_i(\vec{r})H'(\vec{r}-\vec{r}\,')\tau_j(\vec{r}\,')+\int d^3r''\sum_{i\neq j}\sum_{j\neq l}\tau_i(\vec{r})H'(\vec{r}-\vec{r}\,'')\\ \times\tau_j(\vec{r}\,'')H'(\vec{r}\,''-\vec{r}\,')\tau_l(\vec{r}\,')+\cdots\end{aligned} \tag{8}$$

or, in operator form,

$$\mathcal{G}=\sum_i\tau_i+\sum_{i\neq j}\tau_iH'\tau_j+\sum_{i\neq j}\sum_{j\neq l}\tau_iH'\tau_jH'\tau_l+\cdots, \tag{9}$$

where $\tau_i=\delta(r-R_i)/(\omega-H_0)$. Equation (9), while written down for our Green's function, bears a formal analogy with the $T$-matrix expansion[3,6] for an electron in an array of scatterers. $\tau_i$ is analogous to a single-scatterer $T$ matrix $t_i$, and $H'(\vec{r}-\vec{r}\,')$ to the free-electron Green's function. We can exploit this analogy to apply multiple-scattering results to our model. The analog of the scattering potential here is proportional to a $\delta$ function, and this will result in simplifications.

The simplest result to obtain is the quasicrystalline approximation of Lax.[2] The result for the Fourier transform $G_{\vec{k}}$ of $G(\vec{r}-\vec{r}\,')=\langle G(\vec{r},\vec{r}\,')\rangle$ is

$$\begin{aligned}G_{\vec{k}}&=n/(\omega-H_0-nH_{\vec{k}}'),\\ nH_{\vec{k}}'&=n\int d^3r\,g(\vec{r})H'(\vec{r})e^{i\vec{k}\cdot\vec{r}},\end{aligned} \tag{10}$$

where $g(\vec{r})$ is the pair distribution function. This result can be obtained from the statistical average of Eq. (9) by considering only the correlations in position of pairs of atoms corresponding to neighboring indices in each term, as $i,j$ and $j,l$ of the third term, or by the method of Schwartz and Ehrenreich.[3] Note the appearance of a generalization of the Bloch sum.

The density of states per atom is given by

$$N(\omega)=\frac{1}{n}\int\frac{d^3k}{8\pi^3}S_{\vec{k}}\left(-\frac{1}{\pi}\mathrm{Im}G_{\vec{k}}\right), \tag{11}$$

where we assume $\omega$ to have a positive imaginary part. $S_{\vec{k}}$ is the Fourier transform of the overlap integral and provides a natural cutoff for the integral. We calculate the density of states using $H_0=0$ and $H(\vec{r})=H_1S(\vec{r})$ with $S(\vec{r})=\exp(-\lambda r^2)$, i.e., a Gaussian interaction and $H\propto S$. The case $H\propto S$ is, incidentally, the relationship used in the semiempirical extended Huckel theory[9] of molecular orbitals. In both Eqs. (9) and (11) we can relate the Green's function with $H\propto S$ exactly to that for $H'=H$ (i.e., orthogonal orbitals). Thus

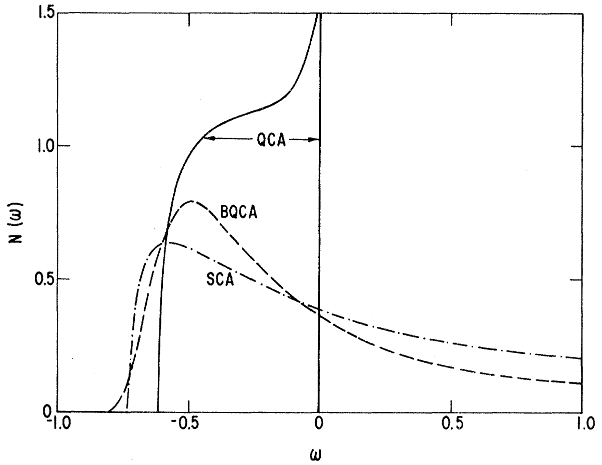

FIG. 1. Density of states for random liquids with $H_0 = 0$, $H(\vec{r}) = H_1 S$, $S = \exp(-\lambda r^2)$, $H_1 = 1$, and $n(\lambda/\pi)^{3/2} = 1.692$. Results as labeled for QCA and SCA; curve labeled BQCA is the result for the broadened QCA for which the width $\gamma_n = 0.7734$.

we can calculate the $H \propto S$ case from the orthogonal orbital Green's function. We have applied this result to a random liquid for which $g(\vec{r}) = 1$ and $nH_{\vec{k}} = nH_1(\lambda/H)^{3/2}\exp(-k^2/4\lambda)$, and the density of states is given in Fig. 1.

For a more realistic model of a liquid metal, we use the pair distribution function corresponding to the exact solution of the Percus-Yevick equation for a hard-sphere liquid, which was shown by Ashcroft and Leckner[10] to give good results for the structure factor in liquid alkalis. We use the Gaussian interaction of the last paragraph, and plot $n\tilde{H}_{\vec{k}}$ for this case in Fig. 2. The solid curve in Fig. 3 is the QCA density of states for this model with $H \propto S$.

We note that there are singularities in the density of states for both cases. These are a consequence of the lack of any level broadening in the QCA for our model, and occur when $dH_k/dk = 0$. For the random liquid, $N(\omega)$ goes as $(ln|\omega|)^{1/2}$ as $\omega \to 0-$. In the hard-sphere case, there is an infinite sequence of inverse-square-root singularities, because $n\tilde{H}_{\vec{k}}$ goes as $(\cos k)/k^2$ for large $k$. The factor $S_{\vec{k}}$, however, weights the integrand in Eq. (12) so that, for the given parameters, only two singularities are evident in Fig. 3. Clearly, a theory which includes damping will remove these singularities.

We discuss here several ways of including damping:

(1) We can relax the condition $\mathcal{H}_{ii} = \text{const}$ and consider the variation of $\mathcal{H}_{ii}$ with its environment.

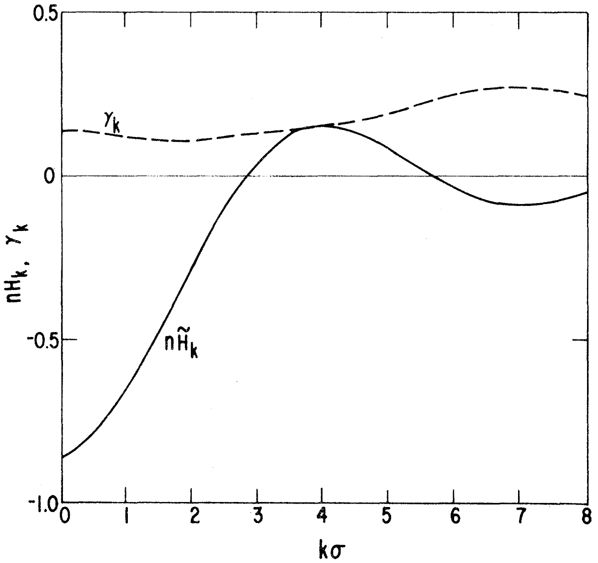

FIG. 2. Energy $n\tilde{H}_{\vec{k}}$ and width $\gamma_k$ versus $k$ for hard-sphere liquids, with $H_0 = 0$, $H(\vec{r}) = H_1\exp(-\lambda r^2)$, $H_1 = 1$, $\lambda = 2$, and $n = 0.859$, in units for which the hard-sphere diameter is 1. This corresponds to a packing fraction of 0.45.

If we average $1/(\omega - \mathcal{H}_{ii})$ instead of $\mathcal{H}_{ii}$, a width will result. We shall not exploit here this method of including damping.

(2) Within the approximation $\mathcal{H}_{ii} = \text{const}$, let us note that the statistical average of Eq. (9) for orthogonal orbitals gives frequency moments of $-\pi^{-1}\operatorname{Im}G(\vec{r}, \vec{r}\,')$ or $-\pi^{-1}\operatorname{Im}G_{\vec{k}}$ about $\omega_0$. The QCA gives the first moment, $n\tilde{H}_{\vec{k}}$, exactly. The second moment depends upon a three-particle distribution function $g(r, r', r'')$. The difference $\gamma_{\vec{k}}^2$ be-

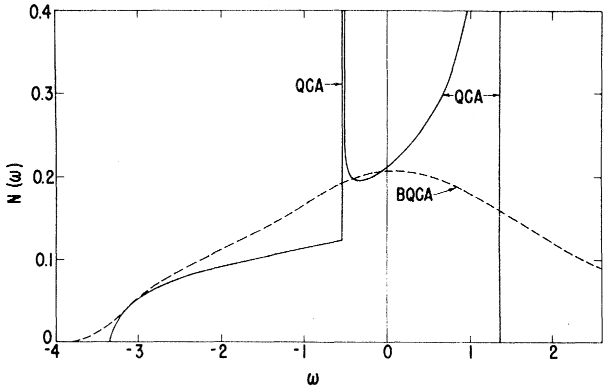

FIG. 3. Density of states for hard-sphere liquids with $H_0 = 0$, $H(\vec{r}) = H_1 S$, $S = \exp(-\lambda r^2)$, $H_1 = e^2$, $\lambda = 2$, and $n = 0.859$, in units for which the hard-sphere diameter is 1. Results are plotted for QCA and BQCA, for which the width $\gamma_{\vec{k}}$ is given in Fig. 2.

tween the second moment and the square of the first gives a measure of the width of the levels. If we use the superposition approximation

$$g(\vec{r},\vec{r}\,',\vec{r}\,'')=g(\vec{r}-\vec{r}\,')g(\vec{r}-\vec{r}\,'')g(\vec{r}\,'-\vec{r}\,''),$$

we obtain

$$\gamma_{\vec{k}}{}^2=n\int\frac{d^3k'}{8\pi^3}\,\tilde{H}_{\vec{k}'}H_{\vec{k}'}+n\int\frac{d^3k'}{8\pi^3}\,h(\vec{k}-\vec{k}\,')\tilde{H}_{\vec{k}'}{}^2, \qquad (12)$$

where $h(\vec{r})=g(\vec{r})-1$. For the random-liquid case, $\gamma_{\vec{k}}$ is thus a constant. For the hard-sphere case we have plotted $\gamma_{\vec{k}}$ in Fig. 2.

We have approximated the spectral function $-\pi^{-1}\,\mathrm{Im}G$ for orthogonal orbitals by a Gaussian with rms deviation $\gamma_{\vec{k}}$. As mentioned above, we use this result to obtain the $H\propto S$ density of states, which is shown in Figs. 1 and 3. We see that the singularities are completely washed out, and that the band edge is lowered and has a tail. The upper end of the band trails off rather slowly.

(3) A third method is to go beyond the QCA. We present here a result for the SCA of Schwartz and Ehrenreich.[3] We again exploit the analogy between our Green's function and the scattering-theory $T$ matrix, and after considerable algebra obtain the equations

$$\begin{aligned}
&G_{\vec{k}}=n/(\omega-H_0-n\tilde{H}_{\vec{k}}-\Sigma_{\vec{k}}),\\
&\Sigma_{\vec{k}}=\int\frac{d^3k'}{8\pi^3}\,\tilde{H}_{\vec{k}}{}'\tilde{H}_{\vec{k}}{}'G_{\vec{k}'}nF(\vec{k}\,',\vec{k}),\\
&nF(\vec{k},\vec{k}\,')=1+nh(\vec{k}-\vec{k}\,')\\
&\qquad\qquad+\int\frac{d^3k''}{8\pi^3}\,h(\vec{k}-\vec{k}\,'')H_{\vec{k}}{}'G_{\vec{k}''}nF(\vec{k}\,'',\vec{k}\,').
\end{aligned} \qquad (13)$$

The SCF Green's function depends on the function $F(\vec{k},\vec{k}\,')$ which obeys an integral equation which is one-dimensional due to isotropy and involves a self-energy $\Sigma_{\vec{k}}$ which needs to be obtained self-consistently. For the special case of a random liquid, $h=0$ and $F=1$, and $\Sigma_{\vec{k}}$ is independent of $\vec{k}$. We have performed the calculation for this case by iteration, and the result is plotted in Fig. 1. We see that this result is qualitatively very similar to the broadened QCA case, but lacks the band tail. We hope to report results for the hard-sphere case in the future.

A special case of interest is that in which the atoms are constrained to lie on a fraction of the sites of a perfect lattice. For the QCA, use of the lattice pair distribution function in Eq. (10) gives

$$G_{\vec{k}}=x/(\omega-H_0-x\epsilon_{\vec{k}}),\quad \epsilon_{\vec{k}}=\sum\nolimits_{\vec{R}}e^{i\vec{k}\cdot\vec{R}}H(\vec{R}). \qquad (14)$$

This corresponds to the average $T$-matrix approximation[6] for the split-band limit of the substitutional alloy. We should note that spurious gaps[5,6] do not occur for the split-band limit.

For the SCA, in addition to using the lattice pair distribution function, we must replace the integrals over $\vec{R}_i$ by sums. The result is Eqs. (13) with $\vec{k}$ going over one Brillouin zone, and with $n$ replaced by $x$, and $nh$ by $-x$. The equations can be reduced to the form

$$\frac{\Sigma-(1-x)(\omega-H_0)}{x}=-\frac{1-x}{\int d^3k\,G_{\vec{k}}/8\pi^3}. \qquad (15)$$

The left-hand side of this equation is the self-energy as defined in the usual treatments of the CPA[5,6] and Eq. (15) is the split-band-limit result.

In conclusion, a tight-binding method is developed for the calculation of electronic states in amorphous systems, and the density of states for simple models of liquid metals is calculated in several approximations. We hope to extend the method to include more orbitals and to allow for consideration of short-range order such as the tetrahedral coordination in amorphous semiconductors.

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