(Each of these papers gives references to other published work in its subject.) The two aspects we predict for threshold behaviour have been observed in some of the reported cases. The prediction for ionization was made earlier by Rudge and Seaton (1964) on the basis of a different approach to this problem.

As long as one obtains an adequate description of an N-electron atom by a product of hydrogenic wave functions, the nature of the two-body potential plus the orthogonality of the wave functions allow the assertion that 'to the lowest order of the mutual interaction of electrons, one incoming electron excites or ionizes only one residual electron at a time'. Consequently, the Peterkop relation in equation (5) and the threshold laws in equations (9) and (10) hold true regardless of the atomic species. The far greater generality of these threshold laws should be tested in the future.

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Generalized coherent-wave approximation for electronic wave functions in a structured liquid

Abstract. The Bloch-like coherent-wave approximation of Phariseau and Ziman can be generalized by inclusion of an operator to take account of the average point-group symmetry of the nearest-neighbour environment in the liquid. It is concluded that liquids with fourfold average co-ordination and a high degree of angular correlation should show unusual electronic properties.

In a recent paper (Fletcher 1967, to be referred to as I) it was shown that the Greenian approach to the treatment of electronic states in liquids (Phariseau and Ziman 1963, Ziman 1966) can be extended, at any rate in the case of a two-dimensional liquid, to take account of angular correlations between nearest-neighbour atoms. The formal results of this treatment allowed important conclusions to be drawn about the existence of band gaps and of bonding–antibonding-type wave functions near the origin in **k** space. It is the purpose of the present letter to show how this formalism can be extended to the three-dimensional case.

The Greenian method assumes a 'muffin-tin' approximation for the potential within a liquid, and brings the integral equation defining the electronic wave function to a manageable form by performing an ensemble average over all configurations of the liquid and by postulating a Bloch-like coherent-wave approximation

$$\psi(\mathbf{x}_{j'}+\mathbf{r}) = \exp\{i\mathbf{k}\,.\,(\mathbf{x}_{j'}-\mathbf{x}_j)\}\psi(\mathbf{x}_j+\mathbf{r}) \tag{1}$$

between the wave functions within atomic cells centred on $\mathbf{x}_j$ and $\mathbf{x}_{j'}$. These assumptions lead to a determinantal equation relating energy and wave vector **k**, real energies being associated with complex wave vectors in a way which may be interpreted as representing scattering from the coherent wave.

The ensemble average involved in this procedure destroys, however, information about any physical effects due to angular correlations amongst nearest neighbours. To preserve this information we note that the set of nearest neighbours will tend, on the average, to have an arrangement characterized by some particular point-group symmetry. We can describe this point group in terms of a regular polyhedron and then define, for each atom in the liquid, the orientation of this polyhedron which best approximates (in an r.m.s. sense) the actual arrangement of its nearest neighbours. This orientation can be specified in terms of a standard orientation $\boldsymbol{\alpha}_0$ by a three-component index $\boldsymbol{\alpha}$ which gives the sequential rotations about three symmetry axes of the point group necessary to pass from $\boldsymbol{\alpha}_0$ to $\boldsymbol{\alpha}$. Instead of making a complete ensemble average in the normal way, we now make such an average relative to the orientation $\boldsymbol{\alpha}$ of the environment of each atom. This gives, for an atom with environmental orientation $\boldsymbol{\alpha}$, a partial ensemble average environment which has the symmetry of the point group used in the classification but which is blurred in both an angular and a radial sense, as discussed for the two-dimensional case in I. The only point groups to survive significantly under this process are the full tetrahedral group T_d, characteristic of fourfold co-ordination, and the full octahedral group O_h, appropriate to six-, eight- or twelvefold co-ordination.

After this partial ensemble average the continuous index $\boldsymbol{\alpha}$ plays the same role in distinguishing atoms with different environments as does the index used to distinguish different atoms in the unit cell in the case of a crystal. The appropriate generalization of (1) is then

$$\psi^{\boldsymbol{\alpha}'}(\mathbf{x}_{j'}+\mathbf{r}) = \exp\{i\mathbf{k}\,.\,(\mathbf{x}_{j'}-\mathbf{x}_j)\}\mathscr{R}_{\mathbf{k}}(\boldsymbol{\alpha}'-\boldsymbol{\alpha})\psi^{\boldsymbol{\alpha}}(\mathbf{x}_j+\mathbf{r}) \tag{2}$$

where the $\mathscr{R}_{\mathbf{k}}(\boldsymbol{\alpha}'-\boldsymbol{\alpha})$ are generalized rotation operators.

The general parametric form of $\mathscr{R}_{\mathbf{k}}(\boldsymbol{\alpha})$ follows from the fact that, if $\boldsymbol{\alpha}_s$ is a symmetry operation of the point group, then

$$\mathscr{R}_{\mathbf{k}}(\boldsymbol{\alpha}_s) = 1. \tag{3}$$

If the directions $\mathbf{u}_i$ about which the components α_i of the rotation $\boldsymbol{\alpha}$ are specified are N_i-fold rotation axes, then it follows that $\mathscr{R}_{\mathbf{k}}(\boldsymbol{\alpha})$ can be expanded as

$$\mathscr{R}_{\mathbf{k}}(\alpha_1, \alpha_2, \alpha_3) = \sum_{n_1 n_2 n_3} a_{n_1 n_2 n_3}(\mathbf{k}) R_{\mathbf{u}_3}(n_3 N_3 \alpha_3) R_{\mathbf{u}_2}(n_2 N_2 \alpha_2) R_{\mathbf{u}_1}(n_1 N_1 \alpha_1) \tag{4}$$

where the n_i are integers, $R_{\mathbf{u}}(\alpha)$ is an elementary rotation operator for a rotation through an angle α about the axis $\mathbf{u}$ and the $a_{n_1 n_2 n_3}(\mathbf{k})$ are numerical coefficients which, in the manner set forth in I, form part of the set of variational coefficients for the Greenian method.

The elementary rotation operators $R_{\mathbf{u}}(\alpha)$ have a simple form in the angular momentum representation (Messiah 1962) and, once an explicit model for the liquid structure has been assumed (as, for example, the model for amorphous germanium proposed by Richter and Breitling 1958), the remaining steps of the Greenian procedure can be carried through as in I.

Important general conclusions, parallelling those for the two-dimensional case, can, however, be drawn without solving or even writing down explicitly these equations. In the case of six-, eight- or twelvefold average co-ordination and point-group symmetry O_h, nearest-neighbour atoms have, on the average, the same orientation $\boldsymbol{\alpha}$. Therefore, by (2) for $\mathbf{k} = 0$, the wave functions on such atoms are on the average the same and we have the liquid analogue of a crystal with one atom per unit cell. On the other hand, for the fourfold co-ordination point group T_d, nearest neighbours are, on the average, related by an inversion operation together with an arbitrary rotation about the common bond direction. However, T_d does not contain the inversion as a symmetry element, so the rotation which is essentially equivalent to it involves a rotation through $\frac{1}{2}\pi$ about one of the twofold symmetry axes $\mathbf{u}_j$ of the point group. The operator $\mathscr{R}$ then involves a linear combination of terms which introduce a change in sign in the wave function (n_j odd), and terms which leave the sign unchanged (n_j even). These two sets can be separated and the wave function broken into two parts with bonding and antibonding character respectively, so that the liquid is the analogue of a crystal with two atoms per unit cell.

Liquids with approximately fourfold co-ordination and a high degree of tetrahedral angular correlation may thus be expected to have electronic structures, near $\mathbf{k} = 0$, similar to those of 4-co-ordinated crystals. As shown in I, however, these singular properties will disappear as the angular correlation of nearest neighbours breaks down.

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