## A Variational Approach to the Unipotential Many-Electron Problem

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SLATER[1] has pointed out the advantage of an approximate solution of the many-electron problem in which all the electrons move in the same potential field. He gave an *ad hoc* formula for constructing such a potential by averaging the Hartree-Fock potentials[2] of the various electrons in a certain way. For the exchange part of the potential, he gave

$$-\frac{\sum_{i,j}\psi_j(\mathbf{r}_1)\psi_i^*(\mathbf{r}_1)\int d\tau_2\psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)/r_{12}}{[\sum_i \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)]}.$$

Slater's work suggests the following variational problem. Find that potential, the same for all the electrons, such that when it, and consequently the wave functions, are given a small variation, the energy of the system remains stationary. A Slater determinant constructed from the one-electron wave functions is used as the wave function of the system.

The potential which fulfills this prescription turns out to be

$$V(\mathbf{r}_1)=V_n(\mathbf{r}_1)+\sum_k\int d\tau_2\frac{\psi_k^*(\mathbf{r}_2)\psi_k(\mathbf{r}_2)}{r_{12}}-W(\mathbf{r}_1), \tag{1}$$

where the exchange potential $W(\mathbf{r})$ is the solution of the integral equation

$$\begin{aligned}\int d\tau_1 W(\mathbf{r}_1)\sum_i\sum_{\alpha\neq i}&\frac{\psi_i(\mathbf{r}_1)\psi_\alpha^*(\mathbf{r}_1)\psi_\alpha(\mathbf{r})\psi_i^*(\mathbf{r})}{E_i-E_\alpha}\\ &=\sum_{i,j}\sum_{\alpha\neq i}\int d\tau_i\frac{\psi_\alpha^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)}{E_i-E_\alpha}\int d\tau_2\frac{\psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)}{r_{12}}\psi_\alpha(\mathbf{r})\psi_i^*(\mathbf{r}).\end{aligned} \tag{2}$$

Here $V_n(\mathbf{r})$ represents the external field acting on the electrons. The $\psi$'s are the solutions of the Schrödinger equation:

$$-\tfrac{1}{2}\nabla^2\psi_\beta(\mathbf{r})+V(\mathbf{r})\psi_\beta(\mathbf{r})=E_\beta\psi_\beta(\mathbf{r}). \tag{3}$$

Greek subscripts refer to all bound solutions of Eq. (3). Roman subscripts refer to occupied levels only. Hartree units[3] are used throughout.

The integral equation (2) can be solved approximately if $E_\alpha$ is replaced by a suitable average value $E_{0i}$. The approximate solution[4] is

$$W(\mathbf{r}_1)=\frac{\sum_{i,j}\frac{\psi_j(\mathbf{r}_1)\psi_i^*(\mathbf{r}_1)}{E_i-E_{0i}}\int d\tau_2\frac{\psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)}{r_{12}}}{\left(\sum_i\frac{\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)}{E_i-E_{0i}}\right)}. \tag{4}$$

Slater's result is obtained from Eq. (4) by making the further approximation that all the $E_i-E_{0i}$ are equal.

Equation (4) is being applied to the quadrivalent state of the carbon atom.

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[1] J. C. Slater, Phys. Rev. 81, 385 (1951).
[2] Actually the potentials averaged differ from the Hartree-Fock potentials in that they are evaluated using Slater wave functions.
[3] Hartree, Proc. Roy. Soc. (London) 141, 282 (1933).
[4] After replacing $E_\alpha$ by $E_{0i}$, the summations over $\alpha$ are allowed to include $\alpha=i$. This implies adding to both sides of the equation terms which would be equal if the Fock exchange potential did not differ from Eq. (4).

## The Electronic Structure of Diamond

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IN a letter under the above title Herman[1] has made several references to a paper of mine[2] in a way likely to cause misunderstanding. He classed the method used as a "tight binding approximation" and suggested that it was inappropriate for valence bands. I should like to make clear that the method of that paper is an equivalent orbital one, first applied to the electronic structure of a solid in that paper, and has no connection, other than an unfortunate superficial resemblance, with any tight binding method.

The equivalent orbital method assumes that the wave function for the crystal is a determinant of orbitals. These orbitals are taken as the best possible ones. The energy contours are then derived using only the transformation properties of such a wave function and the symmetry of the diamond lattice. The second assumption, that only first neighbor equivalent orbitals interact, is not essential to the argument. It can be justified theoretically and empirically but could be relaxed if necessary. The generality of the argument means that the results apply equally to diamond, silicon, or germanium. The difference between these lies in the values of the parameters *a* and *b* and in the presence of extra inner shells.

This equivalent orbital method applies only to the valence bands of diamond, because it is concerned only with the orbitals occupied in the ground state. It says nothing about the conduction bands and, indeed, without some further assumption, these bands cannot even be defined.

In practice all other methods of treating the electronic structure of solids make assumptions like those above and several others in addition. Other methods are analytical, but this is algebraic and so involves no approximate expansions of the orbitals, whether as atomic orbitals or plane waves, no approximate core or exchange potentials, and no difficulties with overlap integrals or boundary conditions.

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[1] F. Herman, Phys. Rev. 88, 1210 (1952).
[2] G. G. Hall, Phil. Mag. 43, 338 (1952).

## Lattice Sums: The Validity of Evjen's Method

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A PARADOX appears in Evjen's method of evaluating the Madelung constant for the cesium chloride lattice.[1] Krishnan and Roy[2] discuss it, amending the choice of unit cell, and giving a general condition for the cell to satisfy. The implication is that the method otherwise fails. Evjen's own argument is no doubt wrong, but it is easily corrected, and the method is actually valid without restriction.

When only finite arrays of charges are considered at each stage, all quantities evaluated are defined by finite sums over the charges, in which we are free to rearrange the terms. In principle, a definite bounding surface exists before such rearrangement, but the principle need not always be explicit. Planes, unit cells, and subcells have all been used to group the charges during summation (Sherman[3] and Frank[4] give detailed references). However, any convenient grouping will in general leave a remainder, of incomplete groups, at the surface. This residual layer may change if the grouping alters, but will prove negligible in determining the energy of a complete group, provided the groups have no dipole moment, and we do not choose one near the surface. The internal potential is, however, sensitive to surface structure, so that the separate contributions of each ion may be changed, although their sum will not. This resolves the paradox in Evjen's paper.[1]

He groups the charges by unit cells (one pair of unlike charges in each), choosing a cube with one charge at the center and the other shared by the eight corners. The array is also a cube, consisting of $n^3$ complete cells, and having a charge of given sign at the center, where Evjen determines the potential. As $n$ is odd or even, this charge lies at the center or the corner of a cell: the outermost charges alternate correspondingly in sign, and the potential is found to oscillate between two separately convergent