=7.5 eV in Eq. (1). More extensive unpublished calculations by these authors bear out our expectation that at larger angles of incidence, $\theta \geq 20°$, the agreement between the model calculations and experimental data has degenerated significantly. We are indebted to Dr. Jepsen, Dr. Marcus, and Dr. Jona for preprints of their results (which were submitted for publication after the submission of this manuscript).

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Calculation of the Physical Properties of Solids by the Extended Huckel Theory

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The philosophical and mathematical justifications for the use of the extended Huckel theory (EHT) in calculating the physical properties of solids are stated, difficulties with the use of EHT in its present form are pointed out, and methods for improving EHT calculations in solids are discussed.

The publication of the paper by Messmer and Watkins[1] on the calculation of the physical properties of diamond and of a nitrogen defect in diamond by the extended Huckel theory (EHT) illustrates once again the usefulness of this simple but elegant quantum-mechanical method of calculating the physical properties of molecules and crystals. EHT[2] is an approximation[3,4] of the rigorous Roothaan-Hartree-Fock[5] (RHF) linear combination of atomic orbitals molecular-orbital self-consistent-field (LCAO-MO-SCF) quantum-mechanical method. As such, there are some limitations in its use, particularly in crystals, most of which, happily, can be overcome. It is our purpose in this paper to state the philosophical and mathematical justifications for the use of EHT, to point out limitations in its use, particularly in crystals, and to suggest improvements to remove these limitations.

Philosophically, the use of EHT is justified because it may be applied at the present time to systems containing at least 200 atomic orbitals, i.e., 50 second- and third-period atoms, or more if hydrogen is one of the constituents, whereas rigorous SCF calculations are still limited to relatively few atoms. Thus many interesting systems are open to study by EHT but not by SCF methods.

The mathematical justification for the use of EHT in calculating the physical properties of molecules (and crystals, small regions of which may be regarded as large molecules) has been adequately described elsewhere.[3,4] Suffice it to say here that the use of EHT in calculating MO wave functions and MO energies is justified because the EHT equations to be solved have exactly the same form as the rigorous RHF[5] equations, i.e., the equations in both cases are

$$\sum_{\beta=1}^{n}(H_{\alpha\beta}-\epsilon_i S_{\alpha\beta})c_{i\beta}=0, \quad \alpha=1\ldots n.$$

In both methods α and β refer to AO's, i refers to MO's, $S_{\alpha\beta}$ are the overlap integrals between the n atomic orbitals χ_α and χ_β, ϵ_i are the MO energies, and $c_{i\beta}$ are the MO coefficients. There are n equations with n terms in each equation. The quantities solved for are ϵ_i and $c_{i\beta}$. In both methods $S_{\alpha\beta}$ are the same; however, in the RHF method $H_{\alpha\beta}$ are complicated functions of the MO coefficients and of two-, three-, and four-center integrals, and this fact necessitates solving the equations by iteration. On the other hand, in EHT the $H_{\alpha\alpha}$ terms are approximated by valence-orbital ionization energies and the $H_{\alpha\beta}$ terms are approximated by the Wolfsberg-Helmholz[6] expression $H_{\alpha\beta}=0.5KS_{\alpha\beta}\times(H_{\alpha\alpha}+H_{\beta\beta})$, or some similar expression. K is a constant usually taken to be between 1.0 and 2.0. If $H_{\alpha\alpha}$ and $H_{\beta\beta}$ have been judiciously chosen, then the EHT equations are quite similar to the last iteration of the RHF equations, and the resulting

MO's and MO energies are virtually the same. It is this fact which mathematically justifies the use of EHT and explains why EHT wave functions are good approximations to RHF wave functions. However, as we shall see, EHT total energies are not good approximations to RHF total energies.

The difficulties with the use of EHT in calculating the physical properties of crystals are of two types: one having to do with the EHT formalism itself and the other having to do with the model of the crystal. In what follows problems (i) and (ii) belong to the first type and problems (iii) and (iv) belong to the second type.

Problem (i) has to do with the way the RHF $H_{\alpha\alpha}$ and $H_{\alpha\beta}$ are approximated by EHT. Newton, Boer, and Lipscomb[3] have examined this question in a series of papers, which now includes other authors,[7] and propose an improvement of EHT which will allow calculation of values of MO coefficients and energies for large systems more nearly equivalent to what the rigorous RHF values would be than the EHT method used by Messmer and Watkins will allow. Lipscomb *et al.* have studied many small-molecule calculations and have concluded that the Hamiltonian matrix elements from small-molecule SCF calculations can be used to calculate the EHT Hamiltonian matrix elements for similar but much larger molecules. They thus avoid the problem of calculating all the necessary integrals for the RHF method but at the same time simulate the exact RHF equations for a large molecule or crystal. They write the diagonal Hamiltonian matrix elements as

$$H_{\alpha\alpha}=\int\chi_\alpha(-\tfrac{1}{2}\nabla^2)\chi_\alpha\,d\nu+V_{\alpha\alpha}$$

and calculate the kinetic-energy term exactly. This term is subtracted from $H_{\alpha\alpha}$, which has been taken from small-molecule calculations, to give $V_{\alpha\alpha}$. They have determined that the Wolfsberg-Helmholtz approximation applies only to the potential energy part of the Hamiltonian matrix elements, so for the off-diagonal elements $H_{\alpha\beta}$ they use the expression

$$H_{\alpha\beta}=\int\chi_\alpha(-\tfrac{1}{2}\nabla^2)\chi_\beta\,d\nu+\text{“}KS_{\alpha\beta}(V_{\alpha\alpha}+V_{\beta\beta})/2\text{”}\ ,$$

where the kinetic-energy term is again calculated exactly. We place the Wolfberg-Helmholz approximation in quotation marks because the exact expression and value of K depend on which atomic orbitals are involved. This improvement is sufficiently simple and important that it ought to be incorporated[4] immediately into all EHT calculations on solids.

Problem (ii) has to do with the way in which the energy of the entire system is calculated. It can be shown that the RHF energy is given by

$$\begin{aligned}E&=2\sum_{i=1}^{N/2}H_i+\sum_{ij}(2J_{ij}-K_{ij})+(N_R)\\&=\sum_{i=1}^{N/2}H_i+\sum_{i=1}^{N/2}\epsilon_i+(N_R)\\&=2\sum_{i=1}^{N/2}\epsilon_i-\sum_{ij}(2J_{ij}-K_{ij})+(N_R).\qquad(1)\end{aligned}$$

The EHT approximation is derived from the third expression where the assumption is made that the electron-electron repulsion terms $\sum_{ij}(2J_{ij}-K_{ij})$ and the nuclear-nuclear repulsion (N_R) terms cancel each other and the energy of the system is equal to twice the sum of the energies of the filled MO's.

The number of situations[1,2,8–12] in which this EHT expression gives good results is embarrassing. The reason it gives any results at all is that the sum of the energies of the filled molecular orbitals

$$2\sum_{i=1}^{N/2}\epsilon_i$$

contains kinetic-energy terms, electron-nuclear attraction terms, and electron-electron repulsion terms, which together can lead to EHT energy minima in a variety of calculations, such as elastic constants and compressibility of crystals,[1,9,10] atom migration energies,[10] Jahn-Teller distortions in crystals,[1,11] barriers to internal rotation in molecules,[2,8] and vibration in molecules.[2,12] The expression is clearly wrong, however, as shown by the fact that molecules such as H_2, Li_2, Be_2, C_2, HF, and HCl do not show any energy minima at all, as the internuclear distance is changed, in EHT calculations.[9] In addition, we found spurious results in our graphite calculations[10] when we moved an interstitial carbon atom too near certain other carbon atoms, i.e., the atoms tended to collapse into one another and the energy of the system became increasingly negative rather than less negative as would be the case if nuclear-nuclear repulsions had been included in the calculations. Other authors have raised similar objections.[13]

One of us has proposed a solution[4] to this problem in which the second part of Eq. (1) is used to calculate the energy of the system. H_i may be written as

$$H_i=\sum_{\alpha\beta}c_{i\alpha}c_{i\beta}\left[\int\chi_\alpha\left(-\tfrac{1}{2}\nabla^2-\sum_{A=1}^{Q}\frac{Z_A}{r_A}\right)\chi_\beta\,d\nu\right],$$

where A refers to the Q nuclei in the system, Z_A is the charge on nucleus A, and r_A is the distance from nucleus A to the electron in question. In addition to the kinetic-energy integrals which have already have been evaluated, this expression requires evaluating electron-nuclear attraction integrals, some of which may involve three centers. Programs for both kinds of integrals are available from the Quantum Chemistry Program Exchange

(QCPE).[14] This improvement should also be incorporated into EHT before further calculations on solids are carried out.

Problem (iii) has to do with the size of the models used in solid-state calculations. We carried out virtually the identical calculation[15] on diamond and on silicon as did MW but abandoned it in favor of graphite because we considered the 35-atom model too small to be meaningful and larger EHT programs were not then available. Our 35-atom model was exactly the same as MW's, although we used slightly different valence-orbital ionization energies for diamond and in the case of silicon appropriate values of the Slater exponents, valence-orbital ionization energies, and lattice constant. We were concerned primarily with the energy of vacancy migration and the energy of Frenkel-pair formation. In the case of silicon we found that moving an atom from 000 to a vacancy at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ required an activation energy of 2.1 eV (000 to $\frac{1}{8}\frac{1}{8}\frac{1}{8}$), but to move an atom from $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ to a vacancy at 000 required an activation energy of 5.4 eV ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$ to $\frac{1}{8}\frac{1}{8}\frac{1}{8}$). Clearly this lack of symmetry is the result of too small a model and it raises questions [beyond problems (i) and (ii)] concerning MW's Jahn-Teller calculation. Their "large molecule" with a defect at the center is suitable for pioneering calculations, but far too small to be anything more. Fortunately, larger EHT calculations have been programmed—we have used a 200 × 200 in our laboratory as opposed to the 140 × 140 used[16] by MW, and even larger ones are on the way. Also judicious use of group theory can easily double or triple the size of the crystal.

Problem (iv) deals with boundary conditions and is closely related to problem (iii). Contrary to the statement by MW that "the success of the EHT method here is related to the uniform charge density over the cluster," neither is the charge density as calculated by EHT uniform over the cluster (as, of course, it should be for the model to be reasonable) nor is the success of EHT related to uniform charge density.[17] Our results on the 35-atom diamond model from a Mulliken population analysis[18] showed the charge to range from 0.38*e* on the central atom through 0.37*e*, 0.17*e*, and 0.06*e* on each successive coordination sphere to − 0.76*e* on the outer (001) atoms. The corresponding values in silicon are 0.39*e*, 0.35*e*, 0.16*e*, 0.06*e*, and − 0.76*e*. The EHT method piles up negative charge on the outside of the molecule in the same fashion as a particle in a spherical-box calculation. In addition to larger models, a technique helpful in reducing the charge differential in covalent crystals is to supply boundary conditions by adding hydrogen atoms at appropriate positions and thereby to remove the loose ends from the cluster. We had no opportunity to do this in our silicon and diamond calculation because we also were limited at that time to 140 atomic orbitals; however, in our graphite calculations[10] we found the carbon-atom charges to be 0.14*e*, 0.31*e*, and − 0.22*e* from the inside out on our 24-carbon-atom model (coronene) without hydrogens, and 0.02*e*, 0.04*e*, and − 0.12*e* on the same carbon atoms when we placed hydrogens in their proper positions at the edge of the structure. The hydrogen charge was 0.09*e*. Proper boundary conditions can thus eliminate large charge differentials at the center of the model.

The success of EHT in MW's paper is related to two factors: (a) EHT MO's and MO energies are closely related to RHF MO's and MO energies if the parameters in the secular equations have been properly chosen, which is the reason for the good agreement of MW's results with the EPR and ENDOR results, for proper grouping of their wave functions into bands, and for the fact that their nitrogen-atom wave function is in the proper place; and (b) EHT total energies contain kinetic-energy, nuclear-electron attraction, and electron-electron repulsion terms, which is often enough to establish an energy minimum, and this is the reason that MW were able to calculate elastic constants and the Jahn-Teller distortion.

EHT has been thoroughly exploited in molecular calculations and the time is now at hand for extending EHT to solid-state calculations on a broad scale. Imaginative calculations such as those of MW coupled with the cautions and improvements discussed here should prove very fruitful.

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Calculation of the Physical Properties of Solids by the Extended Huckel Theory: A Reply

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The general comments of Moore and Carlson[1] with regard to our use of extended Huckel theory (EHT) on a finite molecular cluster to simulate the "deep level" in a semiconductor[2-4] are certainly valid. Improvements in the EHT formalism along the lines they suggest and in other ways, as well as the use of more sophisticated molecular-orbital approaches, should be tried. Similarly, improvements in the model should be made both by increasing its size and by attempting to "tie up" the surface orbitals in some way. In this regard, periodic boundary conditions represent another attractive approach in addition to simply terminating the surface orbitals with hydrogen atoms, as they suggest. We have, in fact, already carried out exploratory calculations with some of these modifications and they will be discussed in a detailed paper currently in preparation. However, it should be pointed out that all such improvements of necessity require considerably more work and hence longer computing times.

There will always be, therefore, strong reasons to use the simplest techniques and the smallest clusters that are sufficient to handle the problem. In view of this let us take this opportunity to reexamine some of the conclusions of Moore and Carlson. In effect, we believe that our model is probably a better approximation to the problem than their arguments may appear to suggest. The reasons for this are as follows: We are not really interested in the properties of the *cluster*. Instead we are interested in the properties of the defect surrounded by the larger bulk crystal. We are using the cluster only as a means of approximating the larger system. This is an important distinction and we believe points (iii) and (iv) made by Moore and Carlson actually have to be modified somewhat in light of this.

In particular, the cluster, because of its surfaces, presents a much more complex environment for the defect than the defect would actually experience in the crystal. For one thing, there will be an elastic "softness" and peculiar polarizability effects associated with the partially filled electronic states near the surface. Also, as mentioned by Moore and Carlson, the charge density will not be uniform. The EHT will therefore not be a very good approximation at all because it is not a self-consistent treatment.

These arguments, however, apply to the *cluster*, not to the defect in the large crystal. In the large crystal, the charge density will tend to be uniform from carbon to carbon, and the EHT approximation to the Fock-matrix elements should therefore be a good one.[5,6] It is this fact which justified the use of EHT for this problem. Arguments based upon a Mulliken population analysis of the *cluster itself*, we believe, are misleading. The charge fluctuations are to a large extent artifacts of the cluster surfaces and are not relevant to the problem of a defect in a real crystal.

The philosophy of our approach then is that we start with a Fock matrix of the order of 10^{22}, which is the real problem of interest—a defect surrounded by the bulk crystal. For this matrix, EHT would give a good approximation for the matrix elements. We then truncate the matrix to a finite size but keep the matrix elements unchanged. We argue that this gives a better approximation for the cluster of atoms in the real crystal than would modification of the matrix elements to account for charge fluctuations that are not actually real.

Second, in our treatment we avoid much of the elastic peculiarities of the surface simply by filling *all* the valence band and surface orbitals of the cluster. (In the cluster calculation, it turns out to be difficult to separate the surface and valence band orbitals anyway.[2]) The arguments of Moore and Carlson in point (iv), on the other hand, apparently result from filling only enough molecular orbitals to make the cluster neutral. Such a pro-