of Chemistry, Indiana University, Bloomington, Ind. 47401.

[15] E. B. Moore, Jr. and C. M. Carlson (unpublished).

[16] MW's program is presumably QCPE 64 or a revised version of it.

[17] Goodisman's paper [J. Goodisman, J. Am. Chem. Soc. 91, 6552 (1969)] is not really applicable here, either the way Goodisman wrote it or the way MW interpreted it.

[18] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955); 23, 1841 (1955); 23, 2338 (1955); 23, 2343 (1955).

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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 procedure leaves unfilled closely spaced states near the top of the valence band which reflect the elastic artifacts of the surfaces. The energy difference they quote (3.3 eV) between the total energy with the vacancy in the 000 and in the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ positions in silicon would probably be substantially less if they followed our procedure. (In the case of the vacancy in diamond, we find our procedure reduces the difference by a factor of 2.)

Our procedure gives a net charge of $-36e$ to a 35-carbon-atom cluster. However, this has no effect at all on the energy levels because the EHT treatment is not a self-consistent one. The molecular-orbital wave functions and energies are independent of the way in which we populate them after the calculation. Actually, however, a Mulliken population analysis does reveal some physical significance to our procedure. One finds that the charge is closely neutral for the central atom and its nearest neighbors. The charge of the atoms in the next two shells (which have one neighbor missing) is $\sim -e$, and in the outer shell (with two missing neighbors) is $\sim -2e$. In effect, we have put an additional electron in each "dangling bond" to saturate it and to simulate the electron contributed by the missing neighbor in the large bulk crystal. If these neighbor atoms were present the extra charges would be on them, and in this sense the charge density is indeed "uniform" on our cluster.

In conclusion, we agree that the EHT method is one that can and should be improved. The surfaces undoubtedly provide complications and it would be desirable to move them farther out by using a larger cluster, or get rid of them entirely by appropriate boundary conditions. However, we believe that the basic EHT approach and the finite cluster, when handled as clarified above, may represent a considerably better approximation to the deep-level problem that is indicated in points (iii) and (iv) of Moore and Carlson. This confusion is no doubt due to the rather terse description of our procedures necessitated by the form of our preliminary communications.[2-4]

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[1] E. B. Moore, Jr. and C. M. Carlson, preceding paper, Phys. Rev. B 4, 2063 (1971).

[2] R. P. Messmer and G. D. Watkins, Phys. Rev. Letters 25, 656 (1970).

[3] G. D. Watkins and R. P. Messmer, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass.* 1970, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1970), p. 623.

[4] R. P. Messmer and G. D. Watkins, Radiation Effects 9, 9 (1971).

[5] G. Blyholder and C. A. Coulson, Theoret. Chim. Acta 10, 316 (1968).

[6] L. C. Allen, in *Sigma Molecular Orbital Theory*, edited by O. Sinanoglu and K. B. Wiberg (Yale U. P., New Haven, Conn., 1970), p. 227.

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Paramagnetostriction of Transition Metals

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Some recent measurements of paramagnetostriction of transition metals are analyzed taking in account the over-all symmetry of the effect, and the possibility of shape paramagnetostriction. It is suggested that the anisotropic effect can explain the rather large experimental values obtained, and that either orbital paramagnetism, or spin-orbit coupling, must be responsible for shape effects.

Some recent measurements of paramagnetostriction of transition metals by Fawcett[1,2] have resulted in surprisingly high values for some metals. For example, the reported values of $\partial \ln\chi/\partial \ln V$ are 14 for Mo, 6.5 for W, 9.6 for Rh, and 22 for Ir. The purpose of this note is to suggest that the interpretation of the measured values in terms of volume dependence of susceptibility is too restrictive, and that one must take in account the tensor character of the phenomenon.

Let us write the free energy of an "initial" volume unit of a metal, assuming cubic symmetry,

$$U = U_0 + \tfrac{1}{2}C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + C_{12}(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy}) + \tfrac{1}{2}C_{44}(e_{yz}^2 + e_{zx}^2 + e_{xy}^2)$$