

Self-Consistent Local Orbitals for Solid Ne, LiH, MgS, and ZnSe†

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In this paper we report on self-consistent local orbitals for a series of materials. This series includes crystals which are molecular in nature, ionic in nature, and rather covalent in nature. In all cases the local-orbitals equations are solved using analytic Hartree-Fock methods. These equations are solved exactly to first order in interatomic overlap. In previous works we have reported solutions for several ionic crystals. The results of these studies are examined and contrasted.

I. INTRODUCTION

In this paper we continue our study of self-consistent localized orbitals for nonmetallic solids.¹ In previous papers we reported results for the LiX systems NaCl, NaBr, KCl, KI and solid Ar. In this paper, we extend this previous work to solid Ne and to LiH. We also report results for MgS and ZnSe. We have reported numerical results for LiH previously; however, here we report analytic results.² As before, we evaluate the local orbitals exactly only to first order in interatomic overlap. It is not *a priori* obvious that such an approximation is valid for ZnSe, a rather covalent substance. None the less, a solution was obtained in order to study this question. This study is discussed in this paper. The results for MgS are of some interest, in that MgS is a basically ionic substance and one thinks of the lattice as containing Mg²⁺ and S²⁻ ions. In free space, the S²⁻ ion is weakly bound at best and may not necessarily be bound in the limit of Hartree-Fock theory. Therefore it is interesting to observe the local orbitals for this ion in a solid environment. In this paper, we find it of interest to study whenever possible the relative distortion of the outer orbitals in the crystalline environment from the free ionic ones, as a function of the dielectric constant. Since this is at best a qualitative question the analysis is performed in a simple way.

In these calculations we use the analytic Hartree-Fock method of Roothaan.³ As in our previous work,¹ we use only a minimum angular basis here. All one-center one-body integrals are evaluated analytically. All one-center two-body integrals are evaluated by numerical means using previously written and accurate codes. All two-center integrals are performed numerically using a program written by one of us (A. B. K.), which uses a double application of Simpson's rule, and is accurate to about six significant figures. In Sec. II the equations used are briefly discussed. In Sec. III the numerical details are presented. Finally these results are analyzed and conclusions are drawn.

II. LOCAL-ORBITALS EQUATIONS AND THEIR SOLUTIONS

In this paper we are concerned with obtaining approximate solutions to the Adams-Gilbert equations.⁴ These equations are

$$(F + \rho A \rho) \phi_{Ai} = \epsilon_{Ai} \phi_{Ai}, \quad (1)$$

where ρ is a spin-independent kernel of the first-order density matrix and is given by

$$\rho(\vec{r}, \vec{r}') = \sum_{Ai, Bj} \phi_{Ai}(\vec{r}) S_{Ai, Bj}^{-1} \phi_{Bj}^\dagger(\vec{r}'). \quad (2)$$

$S_{Ai, Bj}^{-1}$ is the Ai, Bj th element of the inverse of the overlap matrix S whose Ai, Bj th element is $\langle Ai | Bj \rangle$. Using rydberg units, we find that

$$F = -\nabla_1^2 - \sum_I \frac{2Z_I}{|\vec{r}_1 - \vec{R}_I|} + 4 \int \frac{\rho(\vec{r}_2, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 - \frac{2\rho(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \quad (3)$$

In Eq. (1), A is an arbitrary Hermitian operator. In Eq. (3), we use upper-case letters for nuclear coordinates and lower-case letters for electron coordinates.

We approximate Eq. (1) by looking at the ion at site $I=A$. We expand F about A in terms of the complete set ϕ_{Ai} , where this includes virtual orbitals. We also approximate $S_{Ai, Bj}^{-1}$ by $2\delta_{Ai, Bj} - S_{Ai, Bj}$. We also expand $\rho A \rho$ about site A . We then systematically exclude all terms which are quadratic or higher powers in $S_{Ai, Bj}$ for $B \neq A$. This results in the equation

$$(F_A + U_A - \epsilon_{Ai}) \phi_{Ai} = (-\sum_k \sum_j \phi_{Ak} \langle Ak | A | Aj \rangle \phi_{Aj}^\dagger) \phi_{Ai}. \quad (4)$$

It is this equation which we solve here, with

$$A = U_A,$$

$$U_A = -\sum_B \left(\frac{2Z_B}{|\vec{r}_1 - \vec{R}_B|} - 4 \int \frac{\rho_B(\vec{r}_2, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 \right),$$

$$F_A = -\nabla_1^2 - \frac{2Z_A}{|\vec{r}_1 - \vec{R}_A|} + 4 \int \frac{\rho_A(\vec{r}_2, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2$$

TABLE I. In this table, we give the basis used for the calculation of Ne. It was obtained from Bagus (Ref. 5). In order to demonstrate the accuracy of our results, we give the results for the free-atom eigenvalues and eigenvectors obtained using our code and from Ref. 5. For the free-atom case, the C 's given are normalized such that $\int_0^\infty P_{nl}(r) dr = 1$. This is to facilitate comparison with the results of Bagus, who adopts this normalization. The eigenvectors for solid Ne are given also. Here the normalization is $\sum_j C_{nlj}^2 = 1$. Results are in rydbergs. The symbols are defined in the text.

| Basis used | | | | | |
|------------|----------|----------|--|----------|----------|
| j | $l=0$ | | | $l=1$ | |
| | A_{0j} | Z_{0j} | | A_{1j} | Z_{1j} |
| 1 | 0 | 15.439 | | 0 | 10.542 |
| 2 | 0 | 8.806 | | 0 | 4.956 |
| 3 | 2 | 10.995 | | 0 | 2.793 |
| 4 | 1 | 3.764 | | 0 | 1.623 |
| 5 | 1 | 2.301 | | | |

| Free-atom eigenvalues and eigenvectors | | | | | | |
|--|---------------------------|----------------------------|---------------------------|---------------------------|----------------------------|---------------------------|
| j | Reference 5 | | | This work | | |
| | | $\epsilon_{1s1s} = -65.54$ | $\epsilon_{2s2s} = -3.86$ | | $\epsilon_{1s1s} = -65.55$ | $\epsilon_{2s2s} = -3.86$ |
| | $\epsilon_{2p2p} = -1.70$ | | | $\epsilon_{2p2p} = -1.70$ | | |
| j | C_{10j} | C_{20j} | C_{21j} | C_{10j} | C_{20j} | C_{21j} |
| 1 | 0.09218 | 0.00645 | 0.00930 | 0.09245 | 0.00638 | 0.00931 |
| 2 | 0.94891 | -0.28821 | 0.24154 | 0.94860 | -0.28813 | 0.24154 |
| 3 | -0.04499 | -0.02632 | 0.48233 | -0.04485 | -0.02637 | -0.48243 |
| 4 | 0.00308 | 0.56972 | 0.36532 | 0.00320 | 0.56996 | 0.36523 |
| 5 | -0.00003 | 0.53066 | | 0.00000 | 0.53045 | |

| Solid-Ne results | | | |
|------------------|----------------------------|--------------------------------------|-----------|
| | $\epsilon_{1s1s} = -65.55$ | $\epsilon_{1s2s} = -1.70$ | |
| | $\epsilon_{2s2s} = -3.86$ | $\epsilon_{2p2p} = 4 \times 10^{-7}$ | |
| j | C_{10j} | C_{20j} | C_{21j} |
| 1 | 0.09688 | 0.00768 | 0.01427 |
| 2 | 0.99418 | -0.34687 | 0.37081 |
| 3 | -0.04701 | -0.03175 | 0.74019 |
| 4 | 0.00316 | 0.68619 | 0.56073 |
| 5 | 0.00000 | 0.63856 | |

$$-\frac{2\rho_A(\vec{r}_1, -\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|},$$

$$\rho_A(\vec{r}_1, \vec{r}_2) = \sum_i \phi_{Ai}(\vec{r}_1) \phi_{Ai}^*(\vec{r}_2). \quad (5)$$

In Eqs. (4) and (5) summations are over all lattice sites except $A=B$ and over all occupied orbitals about these sites.

The method used to solve Eq. (4) is the analytic Hartree-Fock method of Roothaan.³ Here we use a minimal-angular-basis set and expand ϕ_{Ai} in the form

$$\phi_{Anlm} = Y_l^m(\theta_A, \phi_A) (1/r_A) \sum_j C_{nlj} N_{lj} r^{l+1+A_{lj}} e^{-Z_{lj}r}, \quad (6)$$

$$N_{lj} = [(2Z_{lj})^{2l+2A_{lj}+3} / (2l+2A_{lj}+2)!]^{1/2}.$$

In this type of solution, one chooses a set of A_{lj} and Z_{lj} and then varies the C_{nlj} to minimize the energy. Hence the solution of Eq. (14) becomes a process of matrix formation and diagonalization. In principle, the A 's and Z 's are also varied; however, it is usually possible to borrow a set of A 's and Z 's from previous work or to scale them from

TABLE II. Results of the local-orbitals calculation for Li^+ in LiH are given. Results in rydbergs. The normalization for the solid is $\sum_j C_{nlj}^2 = 1$.

| j | $\epsilon_{1s} = -4.74$ | | |
|-----|-------------------------|----------|-----------|
| | A_{0j} | Z_{0j} | C_{10j} |
| 1 | 0 | 2.69 | 0.84114 |
| 2 | 0 | 4.00 | 0.25366 |
| 3 | 0 | 2.00 | 0.47764 |

such work. In the cases considered here, the use of a minimal angular basis seems reasonable for all but ZnSe which is a tetrahedral system, whereas the others are cubic. None the less, it is included by way of comparison and also as an experiment.

III. DETAILS OF CALCULATION

In this present calculation, we test for self-consistency by comparing the coefficients C of the Slater orbitals for the i th iteration with those from the $(i-1)$ th iteration. When the maximum discrepancy fell below 0.001, the calculations were said to be converged. This level of self-consistency has been found to provide excellent total energies and one-electron wave functions for a variety of atomic cases. The calculations were performed using a code written by one of us (A. B. K.) on the XDS Σ -5 computer in the Materials Research Laboratory and also on the CDC 6600 computer at Wright Patterson Air Force Base.

Wherever possible, we used a basis for the ions which had been obtained previously. For Ne we used the work of Bagus,⁵ for S^{2-} we augmented the basis given by Watson and Freeman,⁶ for Zn and Se the basis given by Watson and Freeman⁷ was used.

In Table I we give our basis for Ne along with the free atomic and the local-orbital eigenvalues and eigenvectors. In this table we include the results of Bagus as a comparison. In Table II we give our basis for Li^+ and the local orbitals for Li^+ in LiH . In Table III we give the basis for H^- and the local orbitals for H^- in LiH . In Table IV we give our basis of Mg^{2+} and the local orbitals for

TABLE III. The local orbitals for the H^- ion in LiH are given. Results in rydbergs. The normalization is $\sum_j C_{nlj}^2 = 1$.

| j | $\epsilon_{1s} = -0.8781$ | | |
|-----|---------------------------|----------|-----------|
| | A_{0j} | Z_{0j} | C_{10j} |
| 1 | 0 | 0.69 | 0.992883 |
| 2 | 0 | 1.50 | 0.081704 |
| 3 | 0 | 0.29 | -0.086643 |

TABLE IV. The basis is defined and the local orbitals are given for Mg^{**} in MgS. The normalization is $\sum_j C_{nj}^2 = 1$. The notation has been defined in the text. Rydbergs are used.

| j | A_{0j} | Z_{0j} | A_{1j} | Z_{1j} |
|-----|-----------------------------|-----------|---|-----------|
| 1 | 0 | 16.459 | 0 | 13.554 |
| 2 | 0 | 10.072 | 0 | 6.450 |
| 3 | 2 | 12.256 | 0 | 3.879 |
| 4 | 1 | 5.004 | 0 | 2.669 |
| 5 | 1 | 3.321 | | |
| | $\epsilon_{1s1s} = -98.118$ | | $\epsilon_{2p2p} = -4.584$ | |
| | $\epsilon_{2s2s} = -7.537$ | | $\epsilon_{1s2s} = -563 \times 10^{-7}$ | |
| j | C_{10j} | C_{20j} | C_{21j} | C_{22j} |
| 1 | 0.20392 | 0.00539 | 0.01047 | |
| 2 | 0.97632 | -0.37669 | 0.34803 | |
| 3 | -0.07219 | -0.02468 | 0.67715 | |
| 4 | 0.00116 | 0.49236 | 0.64825 | |
| 5 | 0.00085 | 0.78425 | | |

Mg^{**} in MgS. In Table V we give our results for S^{--} in MgS. In Table VI we give results for Zn^{**} in ZnSe, and finally in Table VII we give results for Se^{--} in ZnSe. We note that these results for LiH are not directly comparable to those we obtained in the past² owing to the different choices of localizing operator A in the two cases. In this paper we use $A = U_A$ in Eq. (4), whereas in the past we used $A = -U_A$. However, for the ions Se^{--} and S^{--} the choice $A = -U_A$ did not result in localized orbitals,

TABLE V. The basis is defined and the local orbitals given for S^{--} in MgS. The normalization is $\sum_j C_{nj}^2 = 1$ and results are in rydbergs. The notation has been given in the text.

| j | A_{0j} | Z_{0j} | A_{1j} | Z_{1j} | |
|-----|---|-----------|--|-----------|-----------|
| 1 | 0 | 17.8666 | 0 | 12.7980 | |
| 2 | 0 | 13.9239 | 0 | 8.1734 | |
| 3 | 1 | 13.7526 | 0 | 5.0103 | |
| 4 | 1 | 8.9398 | 1 | 3.8107 | |
| 5 | 1 | 6.2464 | 1 | 2.1976 | |
| 6 | 2 | 5.7842 | 1 | 1.5528 | |
| 7 | 2 | 3.0431 | 1 | 0.7790 | |
| 8 | 2 | 2.0549 | 1 | 0.4120 | |
| 9 | 2 | 1.2872 | | | |
| | $\epsilon_{1s1s} = -183.95$ | | $\epsilon_{2s2s} = 82 \times 10^{-7}$ | | |
| | $\epsilon_{2s2s} = -17.947$ | | $\epsilon_{2p2p} = -13.314$ | | |
| | $\epsilon_{3s3s} = -1.8656$ | | $\epsilon_{3p3p} = -0.9117$ | | |
| | $\epsilon_{1s2s} = -554 \times 10^{-7}$ | | $\epsilon_{2p3p} = 396 \times 10^{-7}$ | | |
| | $\epsilon_{1s3s} = -207 \times 10^{-7}$ | | | | |
| j | C_{10j} | C_{20j} | C_{30j} | C_{21j} | C_{31j} |
| 1 | 0.68231 | 0.15845 | 0.03592 | 0.04191 | 0.02143 |
| 2 | 0.72167 | 0.16784 | 0.06666 | 0.33981 | -0.00694 |
| 3 | 0.06636 | 0.19041 | 0.05226 | 0.93917 | 0.30293 |
| 4 | -0.06802 | -0.18130 | -0.06150 | 0.02307 | -0.21377 |
| 5 | 0.06310 | -0.86652 | -0.26244 | 0.01256 | -0.00934 |
| 6 | -0.02432 | -0.35544 | -0.22287 | -0.00665 | -0.89713 |
| 7 | 0.00509 | -0.01941 | 0.38284 | 0.00169 | -0.22551 |
| 8 | -0.00298 | 0.00475 | 0.75012 | -0.00053 | 0.07906 |
| 9 | 0.00740 | -0.00146 | 0.39994 | | |

whereas $A = U_A$ does. Finally we note that in Tables I-VII the energy parameters ϵ_{ij} are determined by the equation

$$\epsilon_{ij} = \langle Ai | F_A + U_A | Aj \rangle. \quad (7)$$

IV. DISCUSSION OF RESULTS AND CONCLUSIONS

The class of materials covered in this report ranges from a highly unpolarizable material Ne ($K_0 = 1.26$) to highly polarizable substances such as MgS ($K_0 = 5.1$) and ZnSe ($K_0 = 5.9$). In the past we have considered systems with intermediate polarizabilities such as Ar ($K_0 = 1.67$), LiCl ($K_0 = 2.75$), LiBr ($K_0 = 3.16$), LiI ($K_0 = 3.80$), and LiF ($K_0 = 1.92$). It seems instructive to observe the change in outer orbitals of the anion as a function of the polarizability or as a function of K_0 .

First, in the case of Ne (Table I) we see that the solid-state local orbitals differ by a trivial amount from the free atomic orbitals. A similar result has been found for Ar,¹ although the changes in Ar are greater than for Ne. In order to make the changes quantitative, we search the outer-orbital-wave-function coefficient table for the free and crystalline solid and find that coefficient C_{nj} changes most. This change is given for several substances as a function of K_0 in Table VIII. Except for the bromides and iodides, it seems clear from Table VIII that the crystal orbitals tend to distort in proportion to the dielectric constant of the medium. This we feel to be especially marked for MgS and ZnSe, where the anions in free space

TABLE VI. The basis and the local orbitals for Zn^{**} in ZnSe are given. The normalization is $\sum_j C_{nj}^2 = 1$ and results are in rydbergs. The notation is defined in the text.

| j | A_{0j} | Z_{0j} | A_{1j} | Z_{1j} | A_{2j} | Z_{2j} |
|-----|------------------------------|-----------|-----------------------------|-----------|---|---|
| 1 | 0 | 31.6557 | 0 | 19.6637 | 0 | 1.8017 |
| 2 | 1 | 27.9415 | 0 | 12.3337 | 0 | 2.9851 |
| 3 | 1 | 14.4013 | 1 | 11.7281 | 0 | 5.3914 |
| 4 | 2 | 13.6516 | 1 | 7.4809 | 0 | 7.9320 |
| 5 | 2 | 6.8235 | 1 | 4.6219 | 0 | 13.5738 |
| 6 | 2 | 5.1970 | 2 | 4.3975 | | |
| 7 | 3 | 5.4626 | 2 | 1.9142 | | |
| 8 | 3 | 2.3494 | 2 | 1.0264 | | |
| 9 | 3 | 1.3648 | 2 | 0.6758 | | |
| 10 | 3 | 0.8829 | | | | |
| | $\epsilon_{1s1s} = -708.358$ | | $\epsilon_{2s2s} = -90.421$ | | $\epsilon_{3s3s} = -12.970$ | $\epsilon_{3d3d} = -3.278$ |
| | $\epsilon_{2s2s} = -90.421$ | | $\epsilon_{3p3p} = -0.9117$ | | $\epsilon_{1s2s} = -643 \times 10^{-7}$ | $\epsilon_{1s3s} = -244 \times 10^{-7}$ |
| | $\epsilon_{3s3s} = -12.970$ | | $\epsilon_{2p2p} = -79.552$ | | $\epsilon_{2s3s} = -76 \times 10^{-7}$ | $\epsilon_{2p3p} = 0.0$ |
| | $\epsilon_{2p2p} = -79.552$ | | $\epsilon_{3p3p} = -9.387$ | | | |
| | $\epsilon_{3p3p} = -9.387$ | | | | | |
| j | C_{10j} | C_{20j} | C_{30j} | C_{21j} | C_{31j} | C_{32j} |
| 1 | 0.99105 | 0.30603 | 0.10235 | 0.16509 | 0.06489 | 0.20045 |
| 2 | 0.12694 | 0.18104 | 0.05751 | 0.98301 | 0.35513 | 0.69232 |
| 3 | -0.01124 | -0.73859 | -0.23965 | 0.07212 | 0.15384 | 0.62915 |
| 4 | 0.00919 | -0.49467 | -0.33189 | 0.03401 | -0.53835 | 0.28681 |
| 5 | -0.01799 | -0.16306 | 0.72237 | -0.00751 | -0.72845 | 0.04923 |
| 6 | 0.03026 | 0.21395 | -0.10403 | 0.00353 | -0.15622 | |
| 7 | -0.01588 | -0.10476 | 0.53363 | -0.00002 | -0.02872 | |
| 8 | 0.00031 | 0.00069 | 0.03000 | -0.00000 | 0.01619 | |
| 9 | -0.00020 | -0.00038 | -0.01662 | 0.00000 | -0.00744 | |
| 10 | 0.00008 | 0.00015 | 0.00663 | | | |

TABLE VII. The basis and the local orbitals used for Se^{2-} in ZnSe are given. The normalization is $\sum_j C_{nj}^2 = 1$ and results are in rydbergs. The notation is given in the text.

| j | A_{0j} | Z_{0j} | A_{1j} | Z_{1j} | A_{2j} | Z_{2j} |
|-----|----------|----------|----------|----------|----------|----------|
| 1 | 0 | 36.2133 | 0 | 22.5809 | 0 | 2.7861 |
| 2 | 1 | 32.1027 | 0 | 14.9893 | 0 | 4.3903 |
| 3 | 1 | 16.7049 | 1 | 14.2061 | 0 | 6.9094 |
| 4 | 2 | 15.8029 | 1 | 9.1689 | 0 | 9.6548 |
| 5 | 2 | 8.1006 | 1 | 5.8363 | 0 | 15.5610 |
| 6 | 2 | 6.3382 | 2 | 5.1943 | | |
| 7 | 3 | 6.5018 | 2 | 2.7166 | | |
| 8 | 3 | 3.3714 | 2 | 1.5552 | | |
| 9 | 3 | 2.1084 | 2 | 1.0866 | | |
| 10 | 3 | 1.4461 | | | | |

| | | | |
|------------------------------|---|---|---|
| $\epsilon_{1s1s} = -922.167$ | $\epsilon_{3p3p} = -13.692$ | $\epsilon_{1s3s} = -258 \times 10^{-7}$ | $\epsilon_{3s4s} = 352 \times 10^{-7}$ |
| $\epsilon_{2s2s} = -121.717$ | $\epsilon_{4p4p} = -1.168$ | $\epsilon_{1s4s} = -51 \times 10^{-7}$ | $\epsilon_{2p3p} = 0.0$ |
| $\epsilon_{3s3s} = -18.231$ | $\epsilon_{3d3d} = -5.669$ | $\epsilon_{2s3s} = -80 \times 10^{-7}$ | $\epsilon_{2p4p} = -30 \times 10^{-7}$ |
| $\epsilon_{4s4s} = -2.074$ | $\epsilon_{1s2s} = -654 \times 10^{-7}$ | $\epsilon_{2s4s} = -45 \times 10^{-7}$ | $\epsilon_{3p4p} = 1306 \times 10^{-7}$ |
| $\epsilon_{2p2p} = -108.916$ | | | |

| j | C_{10j} | C_{20j} | C_{30j} | C_{40j} | C_{21j} | C_{31j} | C_{41j} | C_{32j} |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 | 0.98595 | 0.31661 | 0.13283 | 0.03286 | 0.15872 | 0.05745 | 0.00641 | 0.14941 |
| 2 | 0.1441 | 0.19151 | 0.07782 | 0.01738 | 0.96784 | 0.32327 | 0.09919 | 0.74866 |
| 3 | -0.01900 | -0.73262 | -0.30210 | -0.06798 | 0.19112 | 0.17908 | 0.01607 | 0.56599 |
| 4 | 0.01651 | -0.54537 | -0.43958 | -0.13183 | 0.03947 | -0.38123 | -0.04522 | 0.30680 |
| 5 | -0.03998 | -0.11957 | 0.57793 | 0.39773 | -0.00386 | -0.83954 | -0.33624 | 0.05197 |
| 6 | 0.06234 | 0.11247 | 0.49444 | -0.29101 | 0.00103 | -0.09688 | 0.08466 | |
| 7 | -0.03018 | -0.04182 | 0.33419 | 0.37717 | 0.00024 | -0.02118 | 0.53857 | |
| 8 | 0.00152 | -0.00093 | 0.03667 | -0.57961 | -0.00022 | 0.01004 | 0.54708 | |
| 9 | -0.00087 | 0.00088 | -0.01606 | -0.38873 | 0.00011 | -0.00459 | 0.52747 | |
| 10 | 0.00032 | -0.00036 | 0.00621 | -0.32314 | | | | |

are not found to be bound in the Hartree-Fock limit using our codes. In the case of the bromides and iodides, the deviations are partly masked by the large basis sets employed in the calculation, which permit the distortion to be distributed over a large number of coefficients. Even so, the results within the bromides and within the iodides scale with K_0 .

It is interesting to further examine our worst case ZnSe. First, the assumption of small overlaps is least valid here; second, the environment of a given ion is tetrahedral, which makes our simple basis less than desirable. We have examined the overlaps for nearest and next nearest neighbors in ZnSe and find the largest to be 0.2 using our local orbitals; hence if this is not exactly small, it also is not very large. Second, Euwema⁸ has computed ZnSe charge densities from our orbitals as well as from other methods and finds them to be neither appreciably better nor worse than by any other method.

Finally, we wish to comment upon some recent work on local orbitals, performed by Adams.⁹ In this work Adams argues that the preferable choice for A in our Eq. (4) would be $-U_A$. In this paper we have chosen to use $A = U_A$. Adams argues that the choice $A = -U_A$ will produce orbi-

tals which are least distorted from free atomic orbitals, and that such orbitals are preferable. Adams gives a series of arguments to justify this, which we need not consider at this time. In the majority of cases, we would agree with this conclusion of Adams. However, we find cases, such

TABLE VIII. In this table we present the maximum deviation of an expansion coefficient for a local orbital C_{nj} compared with the equivalent free atomic value for a variety of crystals as a function of the dielectric constant K_0 . Results are for the anion if ionic.

| Substance | K_0 | ΔC_{nj} |
|-----------|-------|--------------------------------|
| Ne | 1.26 | 10×10^{-5} |
| Ar | 1.67 | 4×10^{-2} |
| LiF | 1.92 | 5×10^{-2} |
| NaCl | 2.25 | 7×10^{-2} |
| NaBr | 2.62 | 3×10^{-2a} |
| KI | 2.69 | 2×10^{-2a} |
| LiCl | 2.75 | 6×10^{-2} |
| LiBr | 3.16 | 7×10^{-2a} |
| LiI | 3.80 | 4×10^{-2a} |
| MgS | 5.1 | S^{2-} ion not bound |
| ZnSe | 5.9 | Se^{2-} ion not bound |

^aDeviation masked by large number of basis vectors used in the expansion.

as MgS or ZnSe considered here, where the S^{2-} or Se^{2-} free atomic orbitals are either very diffuse or unbound, and local orbitals which are minimally distorted from the free atomic case would be very diffuse and overlap greatly at best. Such orbitals would be poor choices in many calculations because of their great overlaps. Therefore, we find it desirable in some cases to obtain local orbitals

which are greatly distorted from the free orbitals.

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PHYSICAL REVIEW B

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Direct Optical Observation of the Semiconductor-to-Metal Transition in SmS under Pressure

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A discontinuous change in the reflectivity due to the first-order semiconductor-to-metal transition has been observed in SmS at a pressure of about 6 kbar. The metallic state is characterized by a golden yellow luster which arises because of interband transitions superimposed on the Drude reflectivity. These results and the pressure dependence of the optical-absorption edge in semiconducting SmSe and SmTe are in excellent agreement with earlier resistivity measurements.

Recent resistivity measurements¹ under pressure on SmTe, SmSe, and SmS have revealed that these monochalcogenides undergo a pressure-induced semiconductor-to-metal transition, without involving any change in the crystal structure. This discovery has generated considerable interest in the study of their magnetic² and pressure-volume behavior³ under high pressure, as well as optical studies at atmospheric pressure.^{1,4-6} In this paper we show that the change in reflectivity under *pressure* is one of the most striking phenomena associated with the semiconductor-to-metal transition and in this respect is more spectacular than the resistivity change which can be influenced by extrinsic impurities. In particular, we present for the first time evidence for *metallic* reflectivity in SmS at hydrostatic pressures greater than 6.5

kbar. These results, together with our optical-absorption data taken under high pressure on the insulating state of SmTe and SmSe, provide strong evidence for the interpretation that the semiconductor-to-metal transition in all three compounds arises from *4f*-electron delocalization into the *5d* conduction band and that this is an intrinsic property of the material.

The measurements were made in a hydrostatic-pressure vessel equipped with sapphire windows. Plexol was used as a pressure medium. The reflectivity or absorption data could be taken over the wavelength range 0.26–2.5 μ . The maximum attainable pressure was about 14 kbar.

Figure 1 shows the reflectivity of single-crystal SmS at a fixed wavelength of 0.8 μ as a function of pressure for near-normal incidence. With in-