

**Mulliken-Wolfsberg-Helmholtz band structure of  
di-tetramethyltetraselenafulvalene- $X$  [(TMTSF) $_2X$ ]:  
Role of the basis set**

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We examine the role of the basis set in Mulliken-Wolfsberg-Helmholtz band-structure calculations of di-tetramethyltetraselenafulvalene- $X$  [(TMTSF) $_2X$ ]. We find that for the range of distances involved in intermolecular selenium contacts, it is extremely important to employ extended basis sets that accurately reflect the asymptotic behavior of Hartree-Fock atomic wave functions.

Much attention is currently being devoted to the wide variety of condensed matter phenomena displayed by the superconducting 2:1 Bechgaard salts of TMTSF. This interest has given rise to a number of attempts to calculate the one-electron properties of these compounds by using the semiempirical Mulliken-Wolfsberg-Helmholtz (MWH) technique.<sup>1-6</sup> The first results were obtained by Grant<sup>1,3</sup> and Whangbo, Walsh, Haddon, and Wudl<sup>2</sup> (WWHW), whose band structures gave open, warped, quasi-planar Fermi surfaces. On the other hand, Minot and Louie<sup>6</sup> (ML) recently reported a calculation yielding a very complex and closed Fermi-surface topology, totally different from WWHW and Grant, yet ostensibly with the same calculation technique. The purpose of this Communication is to focus on the central role played by the basis set in MWH band-structure calculations of organic charge-transfer salts. We identify the optimum choice for these materials and conclude that *none* of the published work, going all the way back to tetrathiofulvalimium-tetracyanoquinodimethanide (TTF-TCNQ),<sup>7</sup> employed the most appropriate basis set. We thus report here new representative values of the di-tetramethyltetraselenafulvalene- $X$  [(TMTSF) $_2X$ ] bandwidths and Fermi-surface topological features obtained using the optimal basis set. In addition, we point out that the basis set for selenium chosen by Minot and Louie departs far from presently accepted standards of quantum chemistry knowledge and practice and is the principal source of the difference between their band structure and those of other workers.

It will help to first give a short background discussion of the MWH technique and its dependence on analytical atomic basis sets.<sup>8</sup> The MWH method, sometimes called the extended Hückel method, employs an empirical Hamiltonian based on an idea of Mulliken<sup>9</sup> for approximating the expectation value of an operator in a linear combination of atomic orbitals (LCAO) representation. For the Hamiltonian operator, this approximation takes the form

$$H_{ij} = KS_{ij}(E_{ii} + E_{jj})/2, \quad (1)$$

where  $K$  is a scaling parameter (usually 1.75),  $S_{ij}$  is the overlap matrix element between members of an appropriate basis set, and  $E_{ii}$  denote the one-electron eigenvalues of the basis levels. The basis set functions generally chosen to compute  $S_{ij}$  are Slater-type orbitals (STO's) which potentially constitute a computationally tractable approximation to true one-electron atomic wave functions. By "true atomic wave functions" we mean the best available self-consistent-field (SCF) numerical integration of the atomic Hartree-Fock or Dirac-Fock equations which we can then use to benchmark a given basis set choice. The most general expression for an STO is<sup>8</sup>

$$\varphi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \phi), \quad (2)$$

where

$$R_{nl}(r) = \sum_{\lambda(1)} C_{n\lambda} [(2n_{\lambda})!]^{-1/2} (2\zeta_{\lambda})^{n_{\lambda}+1/2} r^{n_{\lambda}-1} e^{-\zeta_{\lambda}r}. \quad (3)$$

$Y_{lm}(\theta, \phi)$  is the usual normalized spherical harmonic. Equation (3) expresses the radial part of  $\varphi$  as a linear combination of normalized individual STO's where the coefficients  $C_{n\lambda}$  and exponents  $\zeta_{\lambda}$  are variationally computed by self-consistent-field (SCF) techniques to minimize the total atomic electronic energy.

Tables of  $C_{n\lambda}$  and  $\zeta_{\lambda}$  for the elements can be found in several standard reference works.<sup>10-12</sup> The use of only one term in Eq. (3), the so-called single- $\zeta$  approximation, is the common practice of many users of the MWH method for reasons of obvious computational efficiency. Single- $\zeta$  STO's have been the choice in *all* applications to charge-transfer-salt band-structure calculations to date. Since the major contribution to atomic total energy arises from the closed shells, the single- $\zeta$  STO is prejudiced in favor of the inner shells at the expense of outer regions where chemical bonding occurs. However, the optimum basis set for LCAO applications in molecular crystal systems should approximate the asymptotic behavior at large  $r$  of true atomic wave functions as

closely as possible. It turns out that this can be done given the inclusion of enough terms in Eq. (3). The multi- $\zeta$  STO's contained in published tables give radial wave functions that correspond to within a few percent of numerical Hartree-Fock (HF) values at all distances.

Now, what does all this imply for (TMTSF) $_2X$  band-structure calculations?—simply that the basis set closest to HF should be used because the principal distances of interest are between molecules and thus large compared to atomic closed-shell radii. In other words, use multi- not single- $\zeta$  orbitals. The importance of this statement is demonstrated in Fig. 1 which plots  $R_n(r)$  vs  $r$  for the selenium 4s radial wave function and compares the results of numerical HF (or, *vide supra*, multi- $\zeta$  STO) with the single- $\zeta$  basis function used by WWHW and Grant ( $\zeta = 2.44$ ). We see in the 3–4-Å region of major interselenium intermolecular contact in (TMTSF) $_2X$  that, although the amplitude of  $R$  is small, the relative differences are not, amounting to a factor of 4–18 times lower for WWHW over HF. Similar differences are observed for the selenium 4p orbital (WWHW:  $\zeta = 2.07$ ) and represent a general property of single- $\zeta$  STO's. For example, the single- $\zeta$  wave function for carbon is 5–8 times lower than HF in the 3–4-Å region. In passing, we remark that single- $\zeta$  STO's and HF (or multi- $\zeta$  STO's) agree quite well in the 1.5–2-Å region of usual intramolecular bonding—we stress again that it is at intermolecular distances where major differences occur, and therefore the basis set of choice should be multi- $\zeta$  STO's for charge-transfer salts.

All reported single- $\zeta$  (TMTSF) $_2X$  band-structure calculations to date have used more or less the same  $\zeta$  values for carbon and selenium except ML who

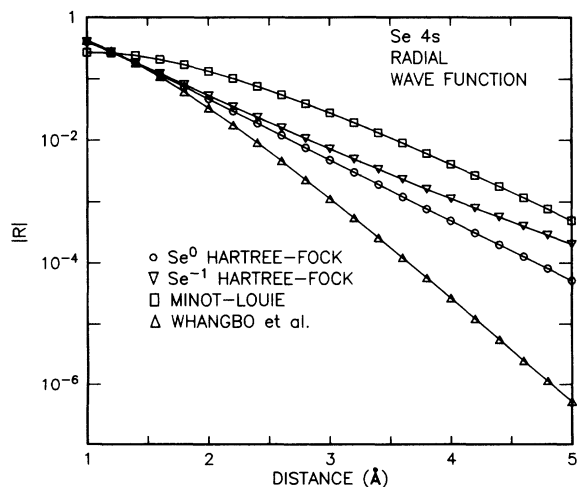


FIG. 1. Comparison of Se 4s Hartree-Fock radial wave functions to the single- $\zeta$  STO values of Whangbo *et al.* (WWHW) and Minot and Louie (ML).

made a quite unusual choice for Se 4s and Se 4p. They state that their value of  $\zeta = 1.473$  for Se was “extrapolated” from “known” values for neutral oxygen ( $\zeta = 2.275$ ) and sulfur ( $\zeta = 1.817$ ).<sup>13</sup> Contrast this number with those obtained by a simple application of Slater's rules which give  $\zeta = 2.42$ , and the SCF optimized values of Clementi and Raimondi<sup>10</sup> which yield 2.44 and 2.07 for Se 4s and Se 4p, respectively. Thus the ML choice for selenium leads via Eq. (3) to a far more diffuse Se valence orbital than would be obtained by any first-principles method. This is apparent by looking again at Fig. 1. The ML Se 4s wave function is 5–8 times higher in amplitude than HF in the region of (TMTSF) $_2X$  intermolecular bonding, whereas we have seen the usual behavior of a normal single- $\zeta$  STO to be about that many times lower. So far we have implied that neutral atom basis sets be used to calculate  $S_{ij}$ . One might argue that if significant charge transfer to Se were to be expected on forming the TMTSF monomer molecule, it would be more appropriate to use a Se<sup>-1</sup> atomic basis set rather than Se<sup>0</sup>. Therefore we also show in Fig. 1 the HF Se<sup>-1</sup> 4s radial wave function which would be the most diffuse selenium orbital one could reasonably expect to arise in the molecule. We see that given even this most improbable charge state, the ML values are still 3–4 times higher. The actual charge on selenium in TMTSF<sup>0</sup> has not been directly determined experimentally. However, indirect evidence suggests that the Se's are only slightly negative.<sup>14</sup> In the TMTSF cationic state, the selenium atoms are probably very close to neutral. In short, there does not seem to be any sound physical basis for the ML choice of the Se 4s  $\zeta$ .

We now discuss the direct effect of  $\zeta$  on the important Se-Se overlap integrals in (TMTSF) $_2X$  which influence through Eq. (1) the major features of its band structure. The results for Se 4s  $\sigma$  overlaps calculated in the three basis sets of Fig. 1 are summarized in Fig. 2. Here we have replaced the HF wave functions with Clementi-Roetti<sup>11</sup> (CR) multi- $\zeta$  STO's which, for all practical purposes, are equivalent to HF. As with the wave functions themselves, the relative differences are huge within the 3–4-Å range of intermolecular contact. For Se 4s, the  $\sigma$  overlaps for WWHW are 2–5 times smaller than CR, and 5–10 times greater for ML. For the Se 4p  $\sigma$  overlaps, the respective ratios are CR/WWHW  $\approx$  2–3 and ML/CR  $\approx$  2–3. Similar results are obtained for the  $\pi$  overlaps. If we compare the relative values of the ML overlaps to the WWHW values, an enhancement in selenium-selenium overlap of over 40 is found. This extraordinary factor is almost solely responsible for the qualitatively very different (TMTSF) $_2X$  band structure found by ML compared to other workers.

The message is clear—completely different band structures in the MWH approximation can be obtained depending on the choice of STO basis set.

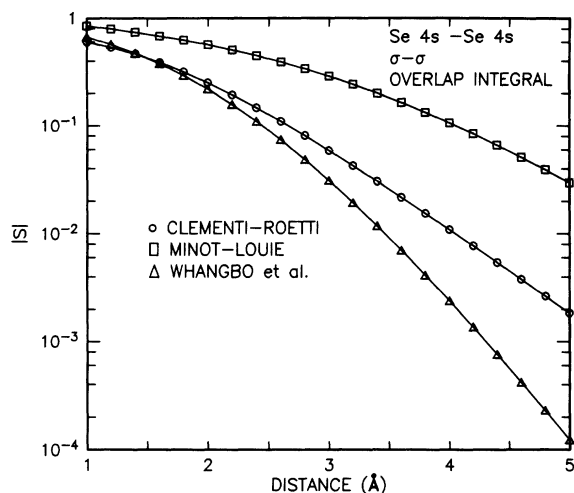


FIG. 2. Comparison of Se 4s  $\sigma$ -overlap integrals for single- and multi- $\zeta$  STO basis sets. See text for details.

The basis sets used for all *ab initio* SCF quantum chemical molecular calculations are those which approximate the Hartree-Fock atomic wave functions as closely as practically possible. *We see no fundamental reason why this practice should not also be followed for semiempirical methods as well.* Accordingly, we have recently completed a recalculation of the band structure of all the  $(\text{TMTSF})_2\text{X}$  compounds of known crystal structure using the best multi- $\zeta$  STO basis sets available. Our findings can be summarized as follows: (1) The cation stack bandwidth increases to about 1.2 eV as compared to 0.6 eV from the single- $\zeta$  calculations of WWHW and Grant, while the transverse bandwidth goes from 50 to around 120 meV. Thus the respective bandwidth values approximately double so that the anisotropy remains the same. (2) Therefore the Fermi surface remains open with topology not much different from the single- $\zeta$  results yielding a warped quasiplanar, two-dimensional contour as found by WWHW and Grant. However, the

greater transverse bandwidth has implications for quasi-one-dimensional fluctuation behavior<sup>15</sup> that go beyond the present discussion.

These new values are in much better agreement with the revised analysis<sup>3,16</sup> of the optical data of Jacobsen *et al.*,<sup>17</sup> the principal experimental probe of the band-structure anisotropy. On the other hand, a simple nearest-neighbor calculation using the ML Se  $\zeta$  yields a stack bandwidth of over 3 eV and a transverse bandwidth of around 0.6 eV,<sup>18</sup> far greater than the experimental plasma energies could give. The diffuse 4s radial wave function leads to a very significant accumulation of charge between first nearest neighbors in the interstack direction (the *I*1 direction of Ref. 3), in contrast to the x-ray results of Wudl *et al.*,<sup>19</sup> who found negligible charge density between cations in this region. We believe these disagreements with experiment arise directly from their particular choice of selenium basis function.

In summary, we have shown the critical importance of the detailed form of the basis set in band-structure calculations of organic crystals using the semiempirical MWH technique. This findings impact all previous band-structure calculations on conducting organic charge-transfer salts, including those of the author.<sup>3</sup> In general, all past estimates of bandwidths in charge-transfer salts will probably have to be revised upwards. Finally, we have shown that the very different  $(\text{TMTSF})_2\text{X}$  band structure arrived at recently by Minot and Louie arises principally from their use of an unusual, and we feel unphysical, selenium valence orbital much more diffuse than that which would be employed in the highest quality quantum chemical calculations.

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<sup>6</sup>C. Minot and S. G. Louie, *Phys. Rev. B* **26**, 4793 (1982).

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<sup>8</sup>An excellent reference on the MWH method and applied quantum chemistry, in general, is S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, *Intro-*

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<sup>10</sup>E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963); single- $\zeta$ ,  $Z \leq 36$ .

<sup>11</sup>E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 177 (1974); multi- $\zeta$ ,  $Z \leq 54$ .

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<sup>13</sup>ML give no details of or references to the extrapolation method employed. The values used for O and S are straight from Slater's rules. We have determined that the O and S  $\zeta$ 's and the ML choice for Se very closely fit the

expression  $\zeta = 0.717 + 4.406Z^{-1/2}$ , where  $Z$  is the atomic number 8, 16, or 34. We are unaware of and have been unable to find the physical basis underlying this particular dependence of  $\zeta$  on atomic number.

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<sup>18</sup>These values were computed using the converged ML results for the valence-state ionization potentials (VSIP) [the  $E_{ii}$ 's of Eq. (1)]. We found the bandwidths were not significantly affected whether starting or converged VSIP's were employed. A cautionary word about charge self-consistency and the MWH method as used by ML: The author has often found (e.g., the H<sub>2</sub>O molecule) that the converged solution does not give as low a total energy as the starting configuration.

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