

band arguments for Pd-Ag. Financial support received from the Science Research Council during a part of this work is also gratefully acknowledged.

¹L. R. Edwards, C. W. Chen, and S. Legvold, *Solid State Commun.* **8**, 1403 (1970).

²J. A. Rowlands and D. Greig, *J. Phys. F: Metal Phys.* **1**, L29 (1971).

³N. F. Mott, *Proc. Phys. Soc., London* **47**, 571 (1935).

⁴B. R. Coles and J. C. Taylor, *Proc. Roy. Soc., Ser. A* **267**, 139 (1962).

⁵H. M. Ahmad and D. Greig, *Phys. Rev. Lett.* **32**, 833 (1974).

⁶R. W. Houghton, M. P. Sarachick, and J. S. Kouvel, *Phys. Rev. Lett.* **25**, 238 (1970).

⁷H. Jones, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1956), Vol. 19, p. 267.

⁸H. P. Myers, L. Wallden, and Å. Karlsson, *Phil. Mag.* **18**, 725 (1968).

⁹C. Norris and P. O. Nilsson, *Solid State Commun.* **7**, 649 (1968).

¹⁰C. Norris and H. P. Myers, *J. Phys. F: Metal Phys.* **1**, 62 (1971).

¹¹P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

¹²B. Kjollerström, *Solid State Commun.* **7**, 705 (1969).

¹³P. Lederer and D. Mills, *Phys. Rev. Lett.* **20**, 1036 (1968).

¹⁴A. B. Kaiser and S. Doniach, *Int. J. Magn.* **1**, 11 (1970).

¹⁵S. Doniach, in "Actinides," edited by J. Darby and A. J. Freeman (Academic, New York, to be published).

¹⁶N. Rivier and V. Zlatić, *J. Phys. F: Metal Phys.* **2**, L87 (1972).

¹⁷W. J. Nellis and M. B. Brodsky, *Phys. Rev. B* **2**, 4590 (1970).

¹⁸H. Montgomery, G. P. Pells, and E. M. Wray, *Proc. Roy. Soc., Ser. A* **301**, 261 (1967).

¹⁹J. S. Dugdale and A. M. Guenault, *Phil. Mag.* **13**, 503 (1966).

²⁰B. R. Coles, *Proc. Phys. Soc., London, Sec. B* **65**, 221 (1952).

Electronic Structure of the Tetracyanoquinodimethane (TCNQ) Molecule

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The electronic structure of an isolated TCNQ molecule has been calculated by the self-consistent statistical-exchange multiple-scattering method. By using overlapping atomic spheres in place of nonoverlapping atomic spheres, a significant increase in physical realism has been achieved. The theoretical model provides a satisfactory account of the photoemission spectra of TCNQ vapor and solid TCNQ. The singlet-triplet splitting for the lowest optical transition is found to be 0.84 eV.

During the past few years, interest in the physics of organic solids has grown rapidly. Of particular interest are highly conducting charge-transfer salts¹⁻³ such as tetrathiofulvalinium-tetracyanoquinodimethanide (TTF-TCNQ).^{4,5} Most current discussions of the physical properties of these organic solids are based on idealized one-dimensional models.¹⁻⁵ However, there are indications⁶ that realistic three-dimensional models are required for a thorough understanding of these properties. Also, conclusive theoretical interpretations of the photoemission spectra of TCNQ vapor and solid TCNQ have not yet appeared.

In this paper we describe a simple theoretical model which can be used to generate realistic energy-level structures for large planar organic molecules such as TCNQ. Our calculations for

the TCNQ molecule were carried out within the general framework of the self-consistent statistical-exchange ($X\alpha$) multiple-scattering method.^{7,8} In an initial effort,⁹ the calculations were carried out on the basis of the standard muffin-tin model^{7,8} by which we mean nonoverlapping atomic spheres embedded in an intersphere region, all surrounded by a bounding outer sphere (cf. Fig. 1). This type of model had been used previously to study other large planar organic molecules.¹⁰ It was clear from the preliminary study of the TCNQ molecule^{9,11} that the standard muffin-tin model was not sufficiently accurate for our purposes, and that a significant improvement in physical realism was necessary if we hoped to deal successfully with the TCNQ molecule.

It is possible to improve upon the standard muffin-tin model by introducing nonspherical terms

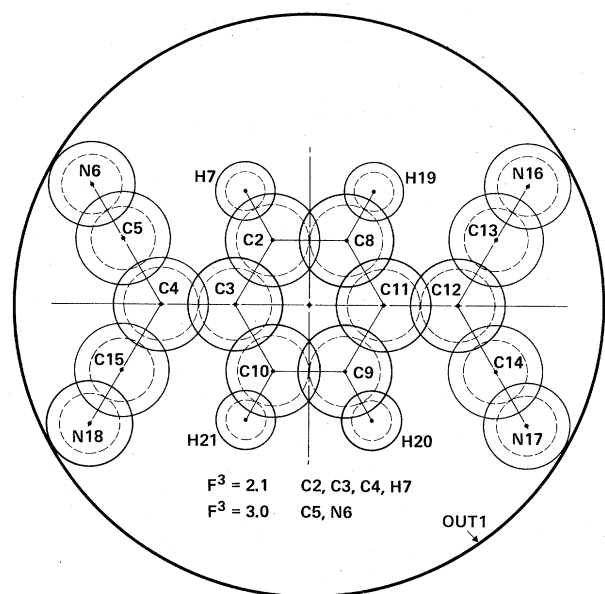


FIG. 1. Nonoverlapping atomic-sphere model (dashed circles) and overlapping atomic-sphere model (solid circles) for the TCNQ molecule. The outer sphere (OUT1) for the former is not shown in the interest of clarity. The outer sphere is assigned serial number 1 and the atomic spheres serial numbers 2 through 21. The ratio of the volumes of the overlapping and corresponding nonoverlapping atomic spheres is denoted by F^3 .

in the atomic spheres as well as nonconstancy terms in the uniform intersphere region.¹²⁻¹⁴ However, these improvements require extensive modification of existing scattered-wave computer programs.^{15,16} Fortunately, one can take a major step^{9,13,17,18} in the direction of improved realism without making any significant changes in existing computer programs. One simply replaces nonoverlapping atomic spheres by overlapping atomic spheres (cf. Fig. 1), and retains the following two simplifying assumptions: (a) Inside each atomic sphere, and outside the bounding sphere, potentials and charge distributions are spherically averaged. (b) In the intersphere region, these quantities are volume averaged. A theoretical justification for this overlapping atomic-sphere model is presented elsewhere,¹³ together with additional information concerning TCNQ calculations based on overlapping atomic-sphere models.

From a practical point of view, the overlapping atomic-sphere model is incomplete until all the atomic-sphere radii (and the outer-sphere radius) are specified. At the present time, the choice of

radii must be dealt with pragmatically. After examining a number of possibilities it was found that substantially the same electronic energy-level structure was predicted by various choices of atomic- and outer-sphere radii, provided these radii were chosen with the following two guidelines in mind: (a) The calculated value of the virial coefficient should be equal to -2 , thereby insuring an optimum balance of potential and kinetic energy within the framework of the present approximations scheme.¹⁹ (b) The calculated value of the first ionization energy should agree with the experimental value. The second guideline is necessary for establishing an accurate absolute energy scale. If one wishes to avoid any appeal to experimental energy-level information, one must greatly refine the existing model and related computer programs. For our purposes, it is more expedient to adjust the radii so that the first ionization energy agrees with experiment.

We will illustrate our results for the isolated TCNQ molecule by considering an overlapping atomic-sphere model having the following attributes: (a) The statistical-exchange parameter α is set equal to 0.75 for all regions of space. (b) The TCNQ molecule is assumed to be planar and to have D_{2h} symmetry. Internuclear distances were obtained by averaging x-ray crystallographic data for the TCNQ crystal²⁰ in accordance with these assumptions, both of which are justifiable in the present context. (c) The choice of nonoverlapping atomic spheres was dictated by the requirements that they touch wherever possible and that (in the case of C5 and N6) they have chemically reasonable proportions.²¹ (d) The outermost sphere was drawn externally tangent to the outermost atomic spheres. (e) The ratio of the volumes of the overlapping and corresponding nonoverlapping atomic spheres for C2, C3, C4, and H7 was 2.1, and for C5 and N6, 3.0. These ratios were chosen so that our two guidelines would be satisfied.

The energy-level structure calculated for this model is shown in Fig. 2 by the long lines. These levels were obtained by the transition-state method^{7,8} so that relaxation effects are taken into account. For purposes of comparison, the results of a recent *ab initio* minimal-basis-set molecular-orbital self-consistent field (MO-SCF) calculation²⁴ are shown by the short lines. In the latter, the energy levels were obtained by taking the differences between the total energies of the ground and ionic states, thereby allowing for relaxation effects. The symmetry notation for the

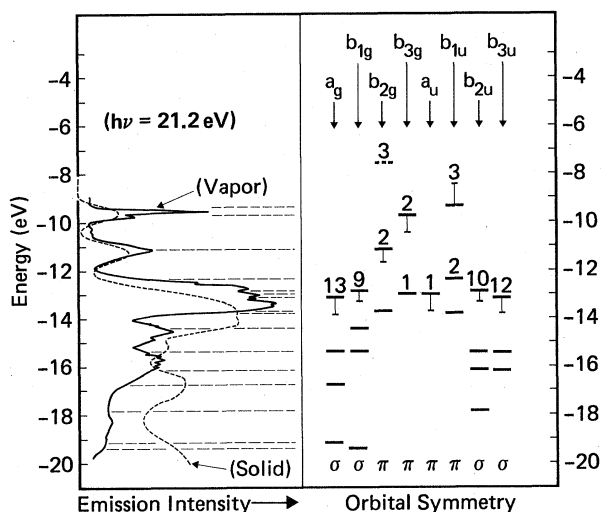


FIG. 2. Comparison of theoretical energy-level structure and experimental photoemission spectra of TCNQ vapor (Ref. 22) and solid TCNQ (Ref. 23). Results of present calculations are shown by the long lines. Results of *ab initio* SCF MO calculation (Ref. 24) are indicated by the short lines. Corresponding energy levels are connected by vertical lines. Occupied levels are denoted by solid lines, unoccupied levels by dashed lines. The symbols σ and π at the bottom right refer to reflection with respect to the plane of the molecule. For each symmetry species, the levels are labeled by serial numbers in order of increasing energy. Only a few of these serial numbers are actually shown.

D_{2h} point group is that of Cotton.²⁵

For all the overlapping atomic-sphere models for TCNQ that have been investigated so far, the two highest occupied levels are invariably $3b_{1u}$ and $2b_{3g}$. These two levels usually lie very close together in energy. Accordingly, the present theoretical model was so chosen that the center of gravity of these two levels would be equal to the experimental value of the first ionization energy, which is given by photoemission measurements for TCNQ vapor as 9.6 eV.²² This spectrum, as well as the photoemission spectrum for solid TCNQ,²³ are reproduced in Fig. 2.

Let us first consider the vapor spectrum for TCNQ since this corresponds more closely to the energy-level spectrum of an isolated molecule. By design, the highest experimental peak at -9.6 eV is attributed to transitions from the two highest occupied levels, $3b_{1u}$ and $2b_{3g}$. The next peak at -11.2 eV is due to transitions from $2b_{2g}$. The small structure on the leading (upper) edge of the large peak at -12.6 eV is due to $2b_{1u}$. The main structure between -12.8 and -14.0 eV is due to

transitions from six levels: $13a_g$, $9b_{1g}$, $1b_{3g}$, $1a_u$, $10b_{2u}$, $12b_{2u}$. The peak at -14.5 eV is probably due to three levels: $8b_{1g}$, $1b_{2g}$, $1b_{1u}$. The peak at -15.8 eV is due to six levels: $12a_g$, $7b_{1g}$, $8b_{2u}$, $9b_{2u}$, $10b_{3u}$, $11b_{3u}$. Contour maps of the electronic charge distributions for representative molecular orbitals of TCNQ are reported elsewhere.^{13,26}

The experimental spectrum for solid TCNQ has been superimposed on the vapor spectrum so that their highest peaks coincide. This was done to illustrate the fact that the two spectra are qualitatively similar, but not everywhere coincident. This lack of coincidence must arise from solid-state effects, i.e., shifts of various levels by slightly different amounts because of interaction with neighboring molecules. If we superimpose the two spectra so that the main peaks are in registry, the vapor peaks at -9.6 and -11.2 eV lie about 0.5 eV below their solid counterparts, and the vapor peak at -15.8 eV lies about 0.5 eV above its solid counterpart. Making allowance for these solid-state shifts, one can interpret the photoemission spectrum for solid TCNQ in the same manner that we interpreted the vapor spectrum above. The magnitude of the solid-state shifts appears to depend on the method of sample preparation, since a comparison of the TCNQ-vapor spectrum with another solid-TCNQ spectrum²⁷ reveals smaller solid-state shifts.

Turning to the excited states we find that the lowest unoccupied level is $3b_{2g}$. The next higher unoccupied levels lie about 2 eV above $3b_{2g}$. In TCNQ⁻ and TCNQ⁻², the $3b_{2g}$ level is singly and doubly occupied. The lowest-energy orbitally allowed optical transition is from $3b_{1u}$ to $3b_{2g}$. A spin-restricted calculation for the present model leads to an excitation energy of 1.9 eV for this transition. A spin-unrestricted calculation leads to a singlet-triplet splitting of 0.84 eV. To obtain a reasonable estimate of the singlet-singlet and singlet-triplet transition energies, we set the center of gravity at 1.9 eV, and weigh the $3b_{2g}$ triplet state three times as heavily as the $3b_{2g}$ singlet state. This leads to an excitation energy of 1.7 eV for the forbidden singlet-triplet transition and 2.5 eV for the allowed singlet-singlet transition. The latter is undoubtedly responsible for the 3.1-eV optical peak observed for TCNQ in solution.²⁸

The present study of the TCNQ molecule thus provides a basis for interpreting optical and photoemission spectra of TCNQ vapor, TCNQ molecules in solution, and solid TCNQ. The physical

realism achieved by adopting the overlapping atomic-sphere model is quite striking. Our work has demonstrated the feasibility of carrying out similar calculations for other large planar organic molecules, and for arrays of such molecules. A companion study of the TTF molecule will be reported elsewhere.²⁹

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*Exchange Professor, Université de Paris VI, September 1973.

¹R. Foster, *Organic Charge-Transfer Complexes* (Academic, London, 1969).

²I. F. Shchegolev, *Phys. Status Solidi (a)* **12**, 9 (1972).

³H. R. Zeller, in *Festkörperprobleme*, edited by H. J. Queisser (Pergamon, New York, 1973), Vol. XIII, p. 31.

⁴A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, *Phys. Rev. B* **5**, 952 (1972); L. B. Coleman, J. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.* **12**, 1125 (1973).

⁵J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Amer. Chem. Soc.* **95**, 948 (1973).

⁶M. H. Cohen, J. A. Hertz, P. M. Horn, and V. K. S. Shante, to be published.

⁷K. H. Johnson, *J. Chem. Phys.* **45**, 3085 (1966); J. C. Slater and K. H. Johnson, *Phys. Rev. B* **5**, 844 (1972); J. C. Slater, *Advan. Quantum Chem.* **6**, 1 (1972); K. H. Johnson, *Advan. Quantum Chem.* **7**, 143 (1973).

⁸K. H. Johnson, J. G. Norman, Jr., and J. W. D. Connolly, in *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1973), p. 161.

⁹F. Herman and I. P. Batra, in *Proceedings of the Colloquium on Many-Electron Effects in Solids*, Taormina, Sicily, Italy, September, 1973 (to be published).

¹⁰D. A. Liberman and I. P. Batra, *J. Chem. Phys.* **59**, 3723 (1973).

¹¹The nonoverlapping atomic-sphere model for TCNQ yielded a virial coefficient of -1.858 (rather than the theoretical value of -2), a first ionization energy of 16.4 eV (experimental value: 9.6 eV), and a set of high-lying occupied energy levels that were much closer together than would be suggested by experimental photoemission spectra.

¹²See for example A. R. Williams and J. van W. Morgan, *J. Phys. C: Proc. Phys. Soc.*, London **7**, 37 (1974).

¹³F. Herman, A. R. Williams, and K. H. Johnson, to be published.

¹⁴J. C. Slater, to be published.

¹⁵K. H. Johnson and F. C. Smith, Jr., Massachusetts Institute of Technology Scattered-Wave Computer Program, July, 1972.

¹⁶D. A. Liberman and I. P. Batra, IBM Research Report No. RJ 1224, 1973 (unpublished). This report documents a modified version of Ref. 15. Still another version of Ref. 15 is documented: J. W. D. Connolly, University of Florida, Gainesville, Report No. 282, 1972 (unpublished).

¹⁷D. A. Liberman, private communication.

¹⁸N. Rösch, W. G. Klemperer, and K. H. Johnson, *Chem. Phys. Lett.* **23**, 149 (1973); N. Rösch and K. H. Johnson, *Chem. Phys. Lett.* **24**, 179 (1974).

¹⁹It is assumed that the TCNQ molecule is in equilibrium for the assigned nuclear coordinates. For a discussion of the virial theorem and the virial coefficient within the context of the statistical exchange approximation, see J. C. Slater, *J. Chem. Phys.* **57**, 2389 (1972).

²⁰R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallog.* **18**, 932 (1965) (TCNQ crystal). The C-H bond distance was taken as 1.09 Å.

²¹J. B. Hendrickson, D. J. Cram, and G. S. Hammond, *Organic Chemistry* (McGraw-Hill, New York, 1970), 3rd ed., p. 58.

²²J. N. A. Ridyard, private communication. The TCNQ-vapor spectrum was obtained with a Perkin-Elmer Model PS 18 spectrometer.

²³W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott, *Phys. Rev. Lett.* **32**, 534 (1974).

²⁴H. T. Jonkman, G. A. van der Velde, and W. C. Nieuwpoort, *Chem. Phys. Lett.* **25**, 62 (1974). Dr. Jonkman has advised the authors in a private communication that his calculation yields a value of 3.68 eV for the first singlet excited state and a value of 3.43 eV for the singlet-triplet splitting. Our singlet-triplet splitting of 0.84 eV appears to be more realistic.

²⁵F. A. Cotton, *Group Theory with Chemical Applications* (Wiley-Interscience, New York, 1971), 2nd ed.

²⁶F. Herman, W. E. Rudge, and I. P. Batra, to be published.

²⁷P. Nielsen, A. J. Epstein, and D. J. Sandman, to be published.

²⁸H. T. Jonkman and J. Kommandeur, *Chem. Phys. Lett.* **15**, 496 (1972).

²⁹B. I. Bennett and F. Herman, to be published.