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TRANSFER INTEGRALS FOR TCNQ SALTS

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Résumé - Les intégrales de transfert sont de grande importance pour la compréhension des propriétés physiques des sels de TCNQ, particulièrement parce que leurs structures cristallographiques varient considérablement. Cette note donne une méthode sûre pour leur calcul.

Abstract - Transfer integrals are of prime importance in understanding the physical properties of TCNQ-salts, particularly since the crystal structures vary widely. This paper gives a reliable method of their calculation.

Introduction

For a fairly long time it has been known that the properties of TCNQ-salts vary widely. Depending on whether one considers 1:1 or 1:2 salts, insulators and metals have been found, $4k_F$ and $2k_F$ phase transitions occur and many different crystal structures have been determined even of chemically very similar compounds. As a case in point we may take the derivatives of R_1R_2 -morpholinium-(TCNQ)₂, where R_1 and R_2 may be varied (note elsewhere in these proceedings the papers of De Boer et al. and Oostra et al. for a review of crystal structures and physical properties).

If one tries to understand the electronic properties on the basis of a Hubbard model one is left with the task to assign values for the transfer integrals t and for the on-site electron-electron repulsion U . The latter is largely an intra-molecular quantity. Some attempts have been made at its estimation (1), experimentally its value is usually also found to be around 1 eV (2). Moreover, it should not vary strongly within a series of TCNQ-salts.

This is not so for the transfer integral t . Particularly since the relevant orbital containing the valence electron in TCNQ⁻ has nodes at right angles to the plane of TCNQ, the transfer integrals should be highly dependent on details of the crystal structure. It therefore appeared worthwhile to construct a simple and reliable computational technique for estimating their value, once the crystal structure is known. This note reports such a technique.

The Model

Our aim will be to compute transfer integrals from

$$t = \sum_{i,j} c_i c_j t_{ij},$$

where the c_i and c_j are the coefficients of the valence orbital on sites i on one ion and sites j on its neighbour and t_{ij} is the transfer integral between two p -functions located at these sites with their z -axes at right angles to the planes of the ions. We should, however, then enquire whether such a procedure is permitted, i.e. whether the slight inter-molecular bonding occurring does not affect the values of c_i , c_j . Or, even if it does, how seriously it then affects the value of t thus calculated. In the following we shall therefore first discuss the various t_{ij} , the two-atom transfer integrals (between two Carbons, Carbon and Nitrogen, and two Nitrogens) then give a fairly simple recipe for the calculation of t_{ij} as a function of distance and angle, then investigate how sensitive our calculation is to intermolecular bonding. We will close with evaluations of t for some morpholinium salts and shortly discuss their properties in the light of the values found.

Calculation of t_{ij}

As the transfer integral deals with the valence electron only, it seems justifiable to consider only the $2p_z$ electron when calculating the atom-atom transfer integral. The $2p_x$ and $2p_y$ orbitals are left out, as they will be used in intramolecular binding, the s electrons are represented by an effective nuclear charge. As a first model system we calculated the intersite transfer in C_2^{2+} . The effective nuclear charge for carbon was taken as 3.6 e (Slater's rules (4)). For the carbon $2p_z$ orbital an STO with exponent 1.568 (5) was used.

The basis set commonly used for the Hubbard Hamiltonian is ($M_s = 0$) (3):

$$\begin{aligned} |1\rangle &= \frac{1}{\sqrt{2}}(C_{1\sigma}^+ C_{2\sigma}^- + C_{2\sigma}^+ C_{1\sigma}^-) |0\rangle \\ |2\rangle &= \frac{1}{\sqrt{2}}(C_{1\sigma}^+ C_{1\sigma}^- + C_{2\sigma}^+ C_{2\sigma}^-) |0\rangle \\ |3\rangle &= \frac{1}{\sqrt{2}}(C_{1\sigma}^+ C_{1\sigma}^- - C_{2\sigma}^+ C_{2\sigma}^-) |0\rangle \\ |4\rangle &= \frac{1}{\sqrt{2}}(C_{1\sigma}^+ C_{2\sigma}^- - C_{2\sigma}^+ C_{1\sigma}^-) |0\rangle \end{aligned}$$

These functions form by definition an orthonormal set. If we want to calculate the constants of the Hubbard Hamiltonian with a quantum chemical procedure we shall have to require the functions used in this procedure to form an orthonormal set as well. Therefore, the two electron functions used in our calculation were subjected first to a Schmidt orthogonalization. We can then evaluate the interaction elements of a 2 electron-2 site system within a VB-CI scheme and construct the interaction matrix which now is formally identical to the interaction matrix obtained by using a Hubbard Hamiltonian:

$$H = U \sum_i n_{i\sigma} n_{i\bar{\sigma}} + \sum_{ij\sigma} t_{ij} (C_{i\sigma}^+ C_{j\sigma}^- + C_{j\sigma}^+ C_{i\sigma}^-)$$

Diagonalization of those matrices gives us the four states of the system ($^1\Sigma_g$, $^3\Sigma_u$, $^1\Sigma_u$, and $^1\Sigma_g$). It was by this procedure that we evaluated the transfer integral. The values for several intersite separations are given in table I.

Table I. Transfer in C_2^{2+} at various internuclear distances

R(Å)	t(eV)
3.175	-0.3326
3.704	-0.0929
4.234	-0.0231

The dependence of t on intersite distance turns out to be nearly exponential for $r \geq 3.0$ Å. The above integrals were calculated for C atoms with $2p_z$ orbitals along the internuclear axis. In molecules, however, this is in general not the case, so we need to introduce a variable ϕ in the calculations. Since the molecules we will consider are generally planar we will only discuss those systems in which at least the z -axes are parallel. This is straightforward but becomes time-consuming as the numerical integration over STO's requires 6 seconds per pair, using the BISON program (6) on a CYBER 176. Fortunately, it turns out that we can fit t to:

$$t(R, \phi) = t(R, \phi = 0) f(\phi)$$

$$t(R, \phi = 0) = t(R_x) \exp(-\alpha(R - R_x)) \quad (1)$$

$$f(\phi) = a + b \cos \phi + c \cos^2 \phi \quad (2)$$

R is the internuclear distance, ϕ the angle between the z axis and the internuclear axis. Values for α , a , b and c are listed in table II.

Table II. Fitting parameters used in the expression for $t(R, \phi)$

	C-C	C-N	N-N
$t(R_x = 3.704 \text{ \AA})$	-0.0929 eV	-0.0646 eV	-0.0260 eV
α	$2.513 \text{ \AA}^{-1}$	$2.608 \text{ \AA}^{-1}$	$3.080 \text{ \AA}^{-1}$
a	-0.002	0.027	0.013
b	0.345	0.247	0.247
c	0.659	0.727	0.741

The same quantities are given for N-N and C-N transfers. The latter were found using an effective nuclear charge of 4.25 (2) and a 2p STO with exponent 1.917 for N. Although C-N does not have inversion symmetry it was treated in the same way, averaging the on-site integrals.

The effect of intermolecular bonding

To investigate the effect of intramolecular bonding a system consisting of two C_2^+ units (C-C distance 1.25 Å), arranged in a rectangle, was studied. CI matrices were obtained at various interunit separation (from 50 000 Å to 3.25 Å) using only two electrons and four orthogonal, interunit mo's (linear combination of $2p_z$ functions).

The results of these calculations were compared with those from a Hubbard Hamiltonian, extended with all inter-site repulsions. The details and results of these efforts will be published elsewhere, suffice it to state here that at $r > 3.28 \text{ \AA}$ inter-unit transfer does not affect the intra-unit bonding sufficiently to affect the value of the transfer integrals significantly. It would seem then, that the procedure given by $t = \sum_{i,j} c_i c_j t_{ij}$ is permissible.

Applications

One of the more interesting TCNQ-salts is TEA (TCNQ)₂. For a review of its properties a paper by Farges (7) can be consulted. Very recently Filhol and Thomas (8) reported structure determinations of TEA (TCNQ)₂ at six temperatures between 40 and 360 K. In fig. 1 we show the result of transfer integral calculations on these structures, using the orbital coefficients of Jonkman, v.d. Velde and Nieuwpoort (9) and the angular and radial dependencies as found in this paper. It is clear that at high temperatures TEA (TCNQ)₂ is electronically dimerized. As the temperature decreases it clearly becomes quarter-

Fig. 1. The ratio's of the transfer integrals in TEA(TCNQ)₂ as a function of temperature.

Finally we apply our calculations to the structures of the (thio)-morpholinium salts of TCNQ. We confine ourselves to the monomeric and dimeric structures. In table III we compare the conductivity with the ratio of the transfer integrals. In general, a higher ratio corresponds to a higher conductivity.

Table III. Conductivities, transfer-ratios and charge ratios of R_1 , R_2 morpholinium (TCNQ)₂ salts.

R_1	R_2	T(K)	$\sigma(\Omega^{-1}\text{cm}^{-1})$	t_1/t_2	ρ_1/ρ_2	ref.
CH ₃	C ₂ H ₅ ^a	348	10	0.94	—	11
H	C ₁₁ H ₉ ^b	300	2.8	0.97	0.39	12
CH ₃	C ₂ H ₅ ^b	300	2.7	0.99	0.50	12
CH ₃	CH ₃ ^b	300	2.2×10^{-3}	0.25	—	12
CH ₃	C ₂ H ₅ ^c	294	1.5×10^{-3}	0.23	0.64	13
CH ₃	CH ₃ ^d	300	2×10^{-3}	0.35		14
CH ₃	CH ₃ ^e	300	5×10^{-5}	0.75	0.10	12

a high temperature phase

b thiomorpholinium derivative

c low temperature phase

d monoclinic structure

e triclinic structure

An exception appears to be dimethylmorpholinium (TCNQ)₂, which is an insulator, even though it has almost equal transfer integrals. Inspection of the crystal structure shows that in this compound the charge is highly localized on one TCNQ ($\rho_1/\rho_2 = 0.10$).

Apparently, in this case the crystal potentials completely localize the charge and prevent it from contributing to the conductivity. It can also be understood then that at very low temperatures it does not show a spin-Peierls transition, but becomes antiferromagnetic (10).

Conclusion

Transfer integrals between TCNQ-ions can be calculated by the procedure

$$t = \sum_{i,j} c_i c_j t_{ij},$$

where the c_i are the coefficients of the valence orbital and the ions i and j . The t_{ij} can be calculated by equations (1) and (2) together with the constants given in Table II. It should be noted that the c_i are taken from calculations for a "free" TCNQ-ion, not for an ion in an actual lattice. It may well be that crystal potentials will affect these coefficients and therefore the transfer integrals. With some numerical effort these effects can be calculated as well and we hope to report on them in a later paper.

References

1. JONKMAN H.T., KOMMANDEUR J., Chem. Phys. Lett. **15** (1972) 496.
2. HIBMA T., SAWATZKY G.A. and KOMMANDEUR J., Phys. Rev. B. **15** (1977) 3959.
3. HARRIS A.B. and LANGE R.V., Phys. Rev. **157** (1967) 295.
4. SLATER J.C., Phys. Rev. **36** (1930) 51.
5. CLEMENTI E. and RAIMONDI D.L., J. Chem. Phys. **38** (1963) 2686.

6. WAHL C., BERTOCINI P.J., KAIZER K. and LAND R.H., "BISON: a Fortran Computer System for the Calculation of Analytic Self Consistent Wavefunctions, Properties, and Charge Densities for Diatomic Molecules". ANL-7271.
7. FARGES J.P., "Physics and Chemistry of Low-D solids", Reidel (Dordrecht) 1980, 223.
8. FILHOL A. and THOMAS M., preprint (1982) to be published in Act. Cryst.
9. JONKMAN H.T., VAN DER VELDE G.A. and NIEUWPOORT W.C., Chem. Phys. Lett. 25 (1974) 62.
10. SCHWERDTFEGER C.F., OOSTRA S. and SAWATZKY G.A., Phys. Rev. B. 26 (1982) 1462.
11. VAN BODEGOM B. and BOSCH A., Acta Cryst. B 37 (1981) 863.
12. VISSER R.J.J., thesis, University of Groningen (to appear).
13. VAN BODEGOM B., Acta Cryst. B 37 (1981) 857.
14. KAMMINGA P. and VAN BODEGOM B., Acta Cryst. B 37 (1981) 114.