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1971

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Joergensen, Christian

### How to cite

JOERGENSEN, Christian. Localized transitions in partly filled shells. In: Mémoires de la Societe Royale des Sciences de Liège, 1971, vol. Série 5, t. 20, p. 335–355.

This publication URL: <https://archive-ouverte.unige.ch/unige:178696>

## LOCALIZED TRANSITIONS IN PARTLY FILLED SHELLS

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### I. IONIZATION ENERGIES

When one speaks about *orbital energy*, it may mean some four or five different quantities [1]. We are here insisting on the *ionization energy*  $I$  which is always defined in an atom, a polyatomic ion or a molecule with access to open, empty space (since the electron with no kinetic energy at large distance from the system considered by definition has the energy zero) and also in a crystal if it is not confined in a closed volume but has access to empty space. The *electron affinity* of an orbital  $a$  is smaller than  $I$ , and to the first approximation, by an integral

$$J(a, a) \sim 0.6 e^2 \langle r^{-1} \rangle_a \quad (1)$$

expressing *interelectronic repulsion*. This expression may either be considered as a *strong-sense integral* where the exact value of the constant, usually between 0.5 and 0.7, depends on the shape of the electronic density of the orbital  $a$ , and where the average value of  $r^{-1}$  is evaluated in atomic units (reciprocal bohr units), or (1) may be considered as a *phenomenological of interelectronic repulsion* [2] which has been decreased (by correlation effects of configuration intermixing) by an additional factor between 0.6 and 0.9 (in monatomic entities with the charge  $z$  having the order of magnitude  $(z + 2)/(z + 3)$  for partly filled shells) which may be thought of as the reciprocal value of an internal dielectric constant for interelectronic repulsion. In neutral atoms, the first ionization energy  $I_1$  has the same order of magnitude as  $J(a, a)$  for  $d$ - and  $f$ -electrons in the five transition groups, and the effects of interelectronic repulsion cannot at all be neglected [3]. As a matter of fact, if  $q$  electrons have to be removed from an atom to form a closed-shell configuration (containing for instance 18, 28, 36, 46, 54, 68 or 86 electrons) the last ionization energy  $I_q$  (if we define  $I_n$  to be the energy difference between  $M^{+n}$  and  $M^{+(n-1)}$  in which case the electron affinity of the neutral atom is  $I_0$ ) is very similar to  $qJ(a, a)$ . Among the various other possible meanings of «orbital energy» is the average  $(I_0 + I_1)/2$  used in Mulliken's definition of electronegativity; the core-ionization energy  $I_q$  just defined, in which case the energy of the neutral atom contains a contribution of  $q(q - 1)/2$  identical or differing  $J(a, a)$  parameters; a somewhat artificial quantity [1] satisfying the virial theorem (that the electrostatic potential energy is  $(-2)$  times the kinetic energy) for the individual orbitals; and finally the one-electron operator energy (with opposite sign) consisting exclusively of attraction between the nucleus and the electrons and of kinetic energy. Though the last alternative might seem the most clear-cut, it is almost impossible to extend to molecules and crystals. Besides the practical difficulty that the observed ionization energies can be far smaller than the pure one-electron quantity (frequently by a factor 10 to 40) a serious disadvantage is that the total interelectronic repulsion energy in a crystal having the extension  $d$  tends to vary as  $d^5$ , as does also the internuclear repulsion, whereas the total bond energy varies as  $-d^3$  being an intensive property. As a matter of fact, the order of magnitude of the total bonding energy is  $-Z^{2.4}$  rydberg units per atom (and rarely more than half a rydberg unit per atom in chemical bonding energy) whereas the rest mass of the electrons according

to Einstein is  $2.137^2 Z$  rydberg units (where we write the reciprocal fine-structure constant  $137.035\dots$  as 137). Hence, a crystal needs not to have  $d$  much above  $30 \text{ \AA}$  before the isolated two-electron operator energy is larger than the rest mass of the electrons, nor much above  $2000 \text{ \AA}$  before it is larger than the rest mass of the nuclei too. Hence, it is necessary to let positive and negative contributions to the electrostatic potential energy coalesce in a kind of *Hartree potential*  $U(x, y, z)$  only having (strongly negative) singularities close to the nuclei and being periodic in unit cells of regular crystals. However, one cannot neglect the effects of interelectronic repulsion (1) if the molecular orbitals are not widely delocalized with concomitant negligible values of  $\langle r^{-1} \rangle$ .

Many solid-state physicists have a great confidence in the *energy band* description introduced by Bloch. In semiconducting crystals with reasonably large energy gap, this is a very unreliable hypothesis seen from the point of view of visible and ultra-violet spectroscopy [1, 4]. On the other hand, metallic materials are in the opposite situation. The highest, partly filled, conduction band consists of highly delocalized orbitals which are the eigen-functions of a Hartree potential which is almost constant in the major part of the unit cell volume and only becomes highly negative in the atomic cores occupying only a small fraction of the volume. In such a case, the reciprocal dielectric constant is effectively zero, quite in contrast to the strongly varying Madelung contribution to the Hartree potential in fairly ionic crystals. The main reason why the energy band description breaks down in non-metallic crystals containing partly filled  $d$ - or  $f$ -shells is equation (1); it becomes a favourable situation to localize a definite positive number of electrons in a partly filled shell  $l^q$  centered around such a transition-group atom in a definite oxidation state (defined [2] from the number  $q$ ) because the two major contributions to the interelectronic repulsion in the electron configuration  $l^q$  are

$$\frac{q(q-1)}{2} A_* + [\langle S(S+1) \rangle - S(S+1)] D \quad (2)$$

The parameter  $A_*$  is closely related to  $J(a, a)$  of eq. (1); its coefficient would be  $(q^2/2)$  in a classical treatment considering the electronic densities as extended, continuous charge distributions. The *spin-pairing energy parameter*  $D$  is about ten times smaller than  $A_*$  and is a definite linear combination [1, 2] of the Slater-Condon-Shortley or Racah parameters of interelectronic repulsion for the  $l$ -shell. The average value of  $S(S+1)$  for the configuration  $l^q$  is

$$\langle S(S+1) \rangle = \frac{3}{4} q \left[ 1 - \frac{q-1}{4l+1} \right] = \frac{3q(4l+2-q)}{16l+4} \quad (3)$$

Equation (2) is a quantitative expression for one of Hund's rules that when a partly filled shell is able to show more than one value of the total spin quantum number  $S$  (i.e. when the shell contains at least two and at most  $4l$  electrons) the groundstate has the *maximum* value for  $S$ . Such behaviour can also be observed in stable molecules formed by elements outside the transition groups. Thus, the oxygen molecule  $O_2$  has  $S=1$  for its groundstate because two orbitals are degenerate of group-theoretical necessity but have only two electrons available though they would have been able to accommodate four electrons (and  $S=0$ ) as known from the peroxide anion  $O_2^-$ . However, such behaviour is far more frequent in the transition group compounds, and the majority of  $3d^5$  manganese (II) and iron (III) complexes have  $S=5/2$  and all known compounds of the isoelectronic series  $4f^7$  europium (II),

gadolinium (III) and terbium (IV) have  $S = 7/2$ . As a matter of fact, the metallic elements and most metallic alloys formed by the 4f-group have so strong a tendency toward localization of a definite number of  $f$  electrons that the conditional oxidation states M(III) or M(II) can be recognized from the magnetic moments indicating  $S$  and hence  $q$ . *Inter-atomic* magnetic coupling effects also dependent on  $S(S + 1)$  (where  $S = 0$  has the lowest energy in the case of anti-ferromagnetic interactions) have been further discussed [5] though the physical origin is another than (2).

In gaseous molecules, the ionization energies of penultimate orbitals are shown by *photo-electron spectroscopy* [6]. Because of the co-excited vibrations, one makes a distinction between *adiabatic transitions* at the minimum energy, where the internuclear distances are allowed to re-arrange, and *vertical transitions* obeying Franck and Condon's principle keeping the internuclear distances constant and simultaneously exciting normal vibrational modes of the excited state. In solids, it is also possible to perform photo-electron spectroscopy [7]. Whereas the measurements on gaseous molecules usually are made with the helium resonance line at 171.13 kK (1 kilokayser =  $1000 \text{ cm}^{-1}$ ) corresponding to 21.2 eV, the surface layers of solids are more conveniently studied with soft X-rays at much higher energy, say 1486 eV. The chemical shifts of the ionization energy of the inner shells can be shown [1] to be very similar to the variation of the ionization energy of the loosest bound electrons. Thus, Basch and Snyder [8] measured the chemical shift of the  $1s$  ionization energy of carbon, nitrogen, oxygen and fluorine in compounds which can run as high as 75 kK, and studies of the penultimate orbitals having ionization energies below 170 kK can be related to ideas of organic chemistry [9]. The comparison of such ionization energies with M.O. (molecular orbital) calculations is of great theoretical interest. For a while, many quantum mechanicians frowned upon the one-electron description of such ionized states. The point is that an atom or a molecule lacking an electron in an inner shell is in a potentially auto-ionizing state high up in the continuum starting at the ionization energy of the loosest bound electron. As we shall see below, the further discussion of excited states shows that there are certain types of one-electron descriptions (essentially finding the eigenvalues in a Hartree potential) which are for better than others for describing the manifold consisting of the groundstate *and* the excited states.

## 2. EXCITATION ENERGIES

It is not generally possible to maintain the simplest conceivable picture of an optical transition from the orbital  $a$  to the orbital  $b$ , that it is the difference  $I(a) - I(b)$  of the two ionization energies. The two main reasons for the discrepancy observed are, in part, compensating each other and are the fact that we need the electron affinity of the orbital  $b$  and that the hole created in the orbital  $a$  colloquially speaking attracts the electron  $b$  to the extent  $J(a, b)$  which is the classical electrostatic interaction between the electronic densities  $\psi_a^2$  and  $\psi_b^2$ . We write the electron affinity of the orbital  $b$  as  $I(b) - J(b, b)$  though  $I(b)$  would not by itself be defined if no electron occupied the orbital  $b$  in the groundstate. In this case,  $I(b)$  is considered to be the sum of the electron affinity of  $b$  and  $J(b, b)$  in order to get a consistent theory. Hence, in all cases, the transition energy is approximately

$$h\nu \sim I(a) - I(b) + J(b, b) - J(a, b) \quad (4)$$

However, if we are studying strongly localized transitions in a partly filled shell

with small average radius  $\langle r \rangle$  the other contributions to the interelectronic repulsion such as the spin-pairing energy proportional to  $D$  of (2) and, in the case of the  $4f$ - and  $5f$ -groups, even relativistic effects as expressed by the Landé spin-orbit coupling parameter  $\zeta_{nl}$  have to be taken into account. We may classify transitions according to decreasing degree of localization :

The lanthanide compounds containing from one to thirteen  $4f$ -electrons have spectra almost like gaseous ions with very narrow absorption bands. Actually, the treatment of the excited levels by the technique of atomic spectroscopy was applied [1, 10] long time before the energy levels belonging to the configuration  $4f^2$  were identified by Sugar in gaseous  $\text{Pr}^{+3}$ . The chemical effects are of two kinds : the degenerate  $J$ -energy levels characterizing spherical symmetry (each consisting of  $(2J + 1)$  states) are slightly split because of the lower local symmetry; and the phenomenological parameters of interelectronic repulsion are decreased to the extent of some 1 to 6 percent [11]. This is called the *nephelauxetic effect* (cloud-expanding effect) because the decrease of  $\langle r^{-1} \rangle$  and increased  $\langle r \rangle$  correspond to adaptation of the radial function of the partly filled shell to a smaller fractional atomic charge (i.e. a less negative central field  $U(r)$  in the Hartree potential) than the oxidation number, and, at the same time, a moderate delocalization of the partly filled shell on the ligands (the neighbour atoms) by formation of anti-bonding M.O. Amusingly enough, Hofmann and Kirmreuther [12] proposed expanded electronic orbits when studying chemical shifts of visible absorption bands of erbium (III) compounds in 1910, three years before N. Bohr's model of the hydrogen atom. At higher wavenumbers, lanthanide compounds may show broad and more intense bands due either to fairly localized  $4f \rightarrow 5d$  transitions (which seem to occur some 10 kK below the value in the corresponding gaseous ions  $M^{+2}$  and  $M^{+3}$ ) or to electron transfer (to be discussed below) from filled M.O. mainly localized on reducing ligands to the empty or partly filled  $4f$  shell.

In the iron ( $3d$ ), palladium ( $4d$ ) and platinum ( $5d$ ) groups, the localized transitions fall in two main classes, the first of which consists of narrow absorption bands showing moderate chemical shifts (due to the nephelauxetic effect; the phenomenological parameters of interelectronic repulsion are 0.25 to 0.94 times as large in  $d$ -group complexes as in the corresponding gaseous ion [2, 13]) and originating in excited levels having almost the same M.O. configuration as the groundstate. Such transitions happen to be spin-forbidden because they go from  $S$  for the groundstate to  $(S - 1)$ , and the main contribution to the energy difference is  $2SD$  from eq. (2). A consequence of the electronic density being almost the same in our three-dimensional space of the excited level and the groundstate (the energy difference is due to increased  $\langle r_{12}^{-1} \rangle$  in the excited state,  $r_{12}$  being the interelectronic distance in the partly filled shell) is that no or very little co-excited vibrations are observed, and that narrow line luminescence frequently can be detected, e.g. the « ruby lines » from the first excited state with  $S = 1/2$  of octahedral *chromophores*  $\text{Cr(III)X}_6$  having  $S = 3/2$  in the groundstate [14]. The isoelectronic  $\text{Mn(IV)O}_6$  can frequently be detected in solid oxides by the luminescent lines in the red. This group of transitions is called *intra-sub-shell transitions* because the  $q$  electrons of the partly filled shell remain in the same sub-shell consisting of degenerate M.O. such as, for instance  $(xy, xz, yz)$  in octahedral  $\text{MX}_6$  where the equivalence of the three Cartesian axes makes it a group-theoretical necessity [15, 16] that the three orbitals have the same energy.

The other class of  $d^q$ -transitions correspond to broad absorption bands. The excited states most frequently have the same  $S$  as the groundstate, and the main

part of the excitation energy is due to a *sub-shell energy difference* such as the anti-bonding orbital ( $x^2 - y^2$ ) colliding with the ligands in octahedral  $\text{MX}_6$  or quadratic  $\text{MX}_4$  relative to a more stable orbital ( $xy$ ) avoiding the ligands to a large extent. The variation of the sub-shell energy difference in octahedral complexes is called the *spectrochemical series* [17]. It is sometimes possible to study the nephelauxetic effect by comparison of two different excited levels belonging to the same excited sub-shell configuration [2, 13]. Because of the great importance of interelectronic repulsion in  $d$ -group complexes, one cannot always conclude that the order of energy levels is simply given by the more or less anti-bonding character making the sub-shell energy differences. Actually, *high-spin* complexes having the opportunity of becoming low-spin by changing to a sub-shell configuration with fewer or no anti-bonding electrons always belong to an apparently excited sub-shell configuration where the stabilization  $-S(S+1)D$  of eq. (2) successfully competes with the sub-shell energy differences. Thus, the two first excited levels of manganese (II) and iron (III) having  $S = 3/2$  belong to a sub-shell configuration containing one anti-bonding electron less than that of the groundstate with  $S = 5/2$ , and correspondingly, the internuclear distances of the minimum of the potential surface of the excited level is *contracted* and sometimes produces a broad-band luminescence.

With the exception of polyatomic ligands changing their number of available lone-pairs ( $\text{NH}_3$  and  $\text{NR}_3$  compared with  $\text{N}_3^-$  or  $\text{NCS}^-$ ; or  $\text{SO}_3^-$  compared with  $\text{RS}^-$ ,  $\text{R}_2\text{NCS}_2^-$  and  $(\text{RO})_2\text{PS}_2^-$ ) the first-neighbour atoms X in a chromophore  $\text{MX}_N$  determine almost exclusively the sub-shell energy difference. Thus, octahedral  $\text{Cr(III)O}_6$  [2, 18] and  $\text{Ni(II)O}_6$  [2, 19] can be studied in the hexa-aqua ion, in complexes of unidentate or multidentate oxygen-containing ligands, in glasses, in dilute solid solution in crystalline mixed oxides (such as the ruby  $\text{Al}_2\text{O}_3$  and the emerald  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  replacing a part of the aluminium atoms) and in stoichiometric compounds such as  $\text{LaCrO}_3$ ,  $\text{MgCr}_2\text{O}_4$ ,  $\text{NiTiO}_3$  and  $\text{NiCO}_3$ . Though the colour varies from green to red in the case of chromium (III) and from yellow to green in the case of nickel (II) as a function of increasing sub-shell energy difference  $\Delta$ , the absorption spectra show a remarkable homogeneity with two and three spin-allowed transitions, respectively. The main reason for the variation of  $\Delta$  seems to be varying Cr - O and Ni - O internuclear distances. Similar effects can be observed [20] by applying high pressures in the region 50000 to 100000 atm. A difference, however, is that high pressure invariably corresponds to a slightly more pronounced nephelauxetic effect, whereas in mixed oxides containing  $\text{Cr(III)O}_6$  the phenomenological parameters of interelectronic repulsion in some cases remain constant and in a few cases increase when the lattice constants of an isomorphous mixture are decreased by substitution of smaller ions for larger ions [2, 18].

The internal transitions in partly filled  $d$ - and  $f$ -shells are treated in *ligand field theory* [17, 21, 22]. Bethe's original *electrostatic model* ascribed the sub-shell energy differences to the non-spherical (small) part of the Madelung potential  $V(x, y, z)$  produced by fractional charges on all the other atoms in the compound considered. As discussed at length at the 10. Solvay Meeting on Chemistry [23] this model is unsatisfactory for many reasons, for instance that neutral polyatomic ligands frequently produce larger sub-shell energy differences than anion ligands, and that small deviations from cubic symmetry were predicted to have far larger effects than actually observed. Even as a starting-point for pedagogic reasons [24], the electrostatic model is entirely unsuitable, in the writer's opinion. However, the feature has remained that the electrons of the partly filled shell are repelled by the ligands. It must be remembered that this shell is formed by the loosest bound orbitals having

*ipso facto* lower electron affinity than the ionization energy of *any* other occupied M.O. Consequently, the *d*- or *f*-like orbitals have to be *orthogonal* on all the previous orbitals according to Pauli's exclusion principle, and the main reason for the sub-shell energy differences seems to be this need for orthogonalization, creating additional radial nodes between M and X in anti-bonding orbitals. It may be noted that the quantitative extent of delocalization is slightly paradoxical in so far that the partly filled shell is more delocalized (as seen from the nephelauxetic effect) in iodide complexes than in fluoride complexes of a given central atom in a definite oxidation state, and also much more delocalized when this oxidation state increases. The point is that in a *bonding* M.O., the electronic density is attracted by the atom having the highest electronegativity, such as F (- I) and M(IV), whereas the anti-bonding M.O. has to be orthogonal on the bonding M.O. of the same symmetry type, and hence, electronic density of the partly filled shell tends to build up on M(II) more than on M(IV) and on iodide more than on fluoride.

In the limit of weak covalent bonding and large differences between the electronegativity of M and X in the chromophore  $\text{MX}_N$  there is a tendency for the anti-bonding energy to be proportional to the square of the (group) overlap integral between the M and the symmetry-adapted  $\text{X}_N$  orbitals. This hypothesis is the basis for the *angular overlap model* which was originally suggested for the very weak chemical effects on the seven *4f*-orbitals in lanthanide compounds [25, 26, 27] and later extended to the more general case of both  $\sigma$ - and  $\pi$ -anti-bonding effects for any *l*-value [28, 29, 30]. It is convenient for calculations that the model is equi-consequential with a singular contact potential acting at the X nuclei. Actually, all of the valid results of ligand field theory can be incorporated in the angular overlap model. Thus, the treatment of *orthoaxial* chromophores having all ligating atoms on the three Cartesian axes can be applied to substituted octahedral complexes, e.g. of chromium (III), cobalt (III) and rhodium (III) [31] but optically active chromophores such as tris (bidentate)  $\text{M}(\text{XX})_3$  can also be treated [32]. If the energy differences in just one *l*-shell are considered without allowing *l*-values of opposite parity to get mixed in, only *holohedrized symmetry* represented by the generated [33] potential  $[\text{U}(x, y, z) + \text{U}(-x, -y, -z)]/2$  is of importance [29, 31]. It is easier to handle linear ligators where the atoms of a polyatomic ligand are situated on a straight line containing the nucleus of the central atom at origo; but it is also possible to extend the angular overlap model to anisotropic non-linear ligators [34].

Ruedenberg [35] analyzed Hellman's old idea that covalent bonding effects can be expressed, to a good approximation, by the *change of kinetic energy in the bond region alone*. Ruedenberg also pointed out that the average radii of the atomic constituents of bonding M.O. tend to contract (in particular in hydrogen compounds) and in anti-bonding M.O. to expand, again connected with the kinetic energy operator. The physical origin of the success of the angular overlap model may again be connected with the change of local contributions to the kinetic energy in the bond region between M and X, the formation of additional radial nodes explaining the increased energy of the anti-bonding orbitals [36, 37].

There is nothing impossible in applying ligand field theory, and in particular, arguments based on the angular overlap model, to *p*-group compounds. Narrow absorption bands are only known in isolated atoms such as thallium (0) formed by irradiation, and in the  $6p^2$ -system bismuth (I) known from molten salts [38]. In complexes having a centre of inversion at a central atom being a halogen or xenon in a positive oxidation state, it is possible [39] to make a distinction between broad but weak bands due to transitions from filled, non-bonding *p*-orbitals to empty

anti-bonding sub-shells, and the much stronger bands which can be classified as electron transfer.

We already mentioned fairly localized  $4f \rightarrow 5d$  <sup>tot</sup>excitations in lanthanide compounds. The transthorium M(III) and M(IV) have similar  $5f \rightarrow 6d$  transitions at somewhat lower wavenumbers. The compounds of tin (II) and antimony (III) have  $5s \rightarrow 5p$  and of thallium (I), lead (II) and bismuth (III) as well as the mercury (0) atom  $6s \rightarrow 6p$  transitions [17, 40, 41]. The mixing of  $l$ -values may be rather serious, and Orgel [42] argued from the stereochemistry that a distortion having cylindrical symmetry occurs, mixing one of the  $p$ -orbitals with the  $s$ -orbital. By the way, arguments can be given for a similar mixing of  $d$ - and  $s$ -character in one orbital of linear (XMX) complexes of copper (I), silver (I), gold (I) and mercury (II) [43, 44]. These cases, as well as the depletion of the electronic density of the filled  $5d(3z^2 - r^2)$  orbital in the equatorial plane of  $\text{PtCl}_4^{2-}$  by mixing with  $6s$ -character [45] are the best authenticated at present for  $l$ -mixing in chromophores. It may be mentioned that whereas the oxidation state of transition group complexes is determined by the number of electrons in the partly filled shell, it is evaluated by analogy in compounds formed by elements outside the transition groups, and it is frequently useful to take stereochemical arguments into account [46].

When talking about the symmetry of a system, it is imperative to think about the time-scale of the experiment. The optical transitions in the visible and ultra-violet are almost instantaneous, and one obtains a picture of considerably lower symmetry than the time-average obtained by X-ray or neutron diffraction crystallography. It has been recognized for a long time that the weak intensities of apparently Laporte-forbidden  $d^q$  or  $f^q$ -transitions are due either to static deviations from a symmetry containing a centre of inversion, or to the accessibility of odd normal modes of vibration of the excited electronic state allowing a small admixture of electron transfer transitions, if these odd normal modes are not already thermally populated in the electronic groundstate. In solution or in vitreous materials, it is not easy to make a distinction between these two alternatives, and it is for instance striking that quadratic palladium (II) complexes have unusually high intensities of their  $4d^8$  inter-sub-shell transitions, and a comparison of the formation constants e.g. for  $\text{Pd}(\text{NH}_3)_2(\text{H}_2\text{O})_2^{+2}$  [47] may suggest a tendency toward *cis*-Pd(II) $\text{X}_2\text{Y}_2$  with inequivalent ligands and the symmetry  $\text{C}_{2v}$  on an instantaneous picture. This is another way of describing  $l$ -mixing to a small extent. Though it is true that refined crystallographic studies allow the determination of anisotropic vibrational average amplitudes and their variation as a function of the temperature, it is by no means easy to exclude that the high symmetry time-average masks a very low instantaneous symmetry [48]. Further difficulties arise from formation of twin crystals or from neglect of weak reflections, both contributing to overestimating the local symmetry. Experiments involving electron or nuclear magnetic resonance involve a time-scale intermediate between the almost instantaneous visible spectroscopy and, say, a millisecond, and it is frequently found by varying the temperature of the sample that a distorted structure of low symmetry is detected by cooling, whereas a higher symmetry of time-average is found at higher temperature.

The halides [39] are in a certain sense in the opposite situation of the immediate post-transition group elements in oxidation states corresponding to the ground configuration  $s^2$ . Thus, alkaline metal halide crystals have local cubic symmetry, and the solutions in water, alcohols, acetonitrile *etc* have almost spherical symmetry. In both cases, the three  $p$ -orbitals remain degenerate, and the only energy separations are due to relativistic effects. There is little doubt today that the first transitions

in bromide are due to  $4p^6 \rightarrow 4p^5 5s$  and in iodide to  $5p^6 \rightarrow 5p^5 6s$ . At somewhat higher energy, the excited configurations  $4p^5 4d$  of bromide and  $5p^5 5d$  of iodide are observed [49]. Similar spectra can be observed of the isoelectronic krypton and xenon atoms in the gaseous state or in cool matrices such as solid argon or thin films of undiluted solid Kr or Xe. Whereas the excitation energies in fairly ionic bromides and iodides are remarkably indifferent to the cation present, the oxides vary quite a lot.  $\text{Cs}_2\text{O}$  is orange, and  $\text{BaO}$  has the  $2p^6 \rightarrow 2p^5 3s$  excitation already in the near ultra-violet at 32.8 kK, incidentally at nearly the same wavenumber as the corresponding transition in the isotopic  $\text{BaS}$  and  $\text{BaSe}$  [50], whereas oxides with large Madelung energy such as  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ThO}_2$  are transparent at much higher wavenumbers and are comparable to crystalline fluorides. Also in tetroxo complexes such as  $\text{MnO}_4^-$  and  $\text{ReO}_4^-$  [51] the  $2p \rightarrow 3s$  transition has so high a wavenumber that it has not been detected. This is *a fortiori* true for  $\text{ClO}_4^-$ , one of the most colourless anions.

It cannot be argued that iodide loses a  $5p$  electron to the solvent unless molecules are present with extraordinarily high electron affinity, such as Kosower's quaternary alkylpyridinium ions. Of course, the statement [39] about  $5p \rightarrow 6s$  transitions in iodide or  $2p \rightarrow 3s$  in oxide does not mean that the radial function of the excited state is very similar to  $6s$  of the neutral iodine atom or  $3s$  of oxygen. It is only meant that the angular function is almost spherically symmetric and at least has no angular nodes, and hence, the « $6s$ » orbital has further on to be orthogonal on the inner shells  $1s$ ,  $2s$ ,  $3s$ ,  $4s$  and  $5s$  of the iodine atom and on all filled orbitals of the surrounding solvent molecules or cations. Again, one must be cautious about the time scale. It may be that the excited configuration  $5p^5 6s$  once formed decays slowly with the transfer of an electron to the solvent either in the form of a solvated electron or in the later step consisting of evolution of molecular hydrogen. The photochemical aspects of the excited state should not be mixed up with the nature of the almost instantaneous excitation by the ultra-violet radiation.

Phillips [52] argues that the energy band description is suitable also in the case of optical excitation of  $\text{KBr}$  or  $\text{RbI}$ . It is true that in sufficiently covalent crystals, such as  $\text{AgBr}$ ,  $\text{ZnO}$ ,  $\text{CdS}$  and  $\text{CdSe}$ , one finally observes a mobility of the optical excitation, and it is argued that *excitons* can be observed corresponding to Rydberg-like series just before the «fundamental» absorption edge. There is no doubt that excitons have been observed in  $\text{Cu}_2\text{O}$  [53] and in various organic crystals; but on the whole, their presence has been overestimated. The optical excitation of fairly ionic bromides and iodides [39, 49] seems to be localized, and the first step of the excitation seems indeed to be appropriately described as  $4p \rightarrow 5s$  and  $5p \rightarrow 6s$ , respectively. Then, the evolution with time in the following microseconds may be different according to the cations present. In alkali metal halides, the external ionization energy, i.e. the threshold energy for Einstein's *photo-emission*, is almost the same as the internal ionization energy, i.e. the threshold for *photo-conductivity*. In the case of iodides, the two lower limits are between the two first strong absorption bands and look suspiciously like  $5p \rightarrow 6p$  excitation. The situation is entirely different in typical semi-conductors such as elemental silicon and germanium, where the «energy gap» or lower limit for photo-conductivity is some 20 kK below the threshold energy for photo-emission. In metallic materials, the internal ionization energy is zero whereas the external ionization energy is the «work function» frequently between 20 and 40 kK ( $1 \text{ eV} = 8.07 \text{ kK}$ ). It is by no means clear whether the energy band model has any connection with the ultra-violet spectra of alkali metal halide crystals. Along this line of thought, it must be realized that liquids

and vitreous materials do not possess energy bands (because they do not repeat a unit cell structure) but can be metallic, semi-conducting *etc* and show the same type of spectra as crystals though the absorption bands usually are somewhat broader under equal external circumstances. It is quite conceivable that the (rather detailed) visible and ultra-violet spectra of thin samples of silicon or copper metal can be described by the energy band model; but there is also much evidence [54] that the absorption spectra of semi-conducting materials with a moderately large energy gap frequently can be ascribed to fairly localized transitions. There is no contradiction in a localized excitation producing a photo-conductive situation; this may, for instance, be promoted by a slight re-adaptation of the internuclear distances around the defect introduced in the regular crystal structure by the optical excitation. One should not forget that the electronic dipole moment whose square contributes to the probability and oscillator strength of the transition  $a \rightarrow b$  can only be obtained by the coexistence of the two orbitals  $a$  and  $b$  in our three-dimensional space. It is true that the « plasma » behaviour of the conduction electrons in a metal, or the near-infra-red absorption of « charge carriers » in non-stoichiometric semi-conductors (such as brown CdO and  $\text{Tl}_2\text{O}_3$ ) can induce delocalized transitions; but it is probable that localized excitations are far more common than believed by many solid-state physicists.

*Electron transfer spectra* are normally produced by a chromophore containing a reducing ligand X with low ionization energy of the highest filled orbital and an oxidizing central atom M having empty or partly filled orbitals with a high electron affinity. The existence of such transitions was already recognized by Rabinowitch [55] and Linhard and Weigel [56], but obviously, their theoretical treatment could not be fruitfully developed before the understanding of internal transitions in partly filled shells. A numerous and coherent class of complexes having electron transfer bands is the octahedral hexahalides  $\text{MX}_6^{z-6}$  containing the central atom M in the oxidation state  $+z$  [57]. The treatment has been further refined [58] taking relativistic effects in the ligands and ligand-ligand anti-bonding effects more explicitly into account. The identification of the individual symmetry types of  $X_6$  orbitals has been slightly modified [59] using the *Faraday effect*, i.e. the optical activity induced in the complex by an external, strong magnetic field. The colourless cations A in  $\text{A}_2\text{MX}_6$  induce a moderate shift of the electron transfer bands of  $\text{MX}_6^-$  (of the  $5d$  group) which can be interpreted as a small variation of the M — X distance [60] like in Drickamer's high-pressure experiments [20] where the shift toward *lower* wavenumbers indicates increasing inter-ligand anti-bonding. The numerous energy levels for M = Os and Ir have been further parametrized [61].

It is rather surprising that the wavenumber of the first Laporte-allowed electron transfer band varies so regularly with the halide  $X^-$  and with M in a definite oxidation state. One would have expected that the Madelung potential would have a strong influence on the excitation energy of the halide ligands, as it actually has to a certain extent on oxides [62, 63]. However, it is possible [1] to introduce the *optical electronegativity*  $x_{\text{opt}}$  from the regularities in the hexahalide electron transfer spectra

$$\sigma_{\text{corr}} = [x_{\text{opt}}(X) - x_{\text{opt}}(M)] \cdot 30 \text{ kK} \quad (5)$$

where  $\sigma_{\text{corr}}$  is the wavenumber of the first Laporte-allowed band corrected by subtraction of  $\Delta$  in the case where the transition goes to the higher, anti-bonding sub-shell, and also corrected for the (numerically rather minor) effects of the spin-pairing energy (2). The optical electronegativities of the halides are 3.9 of F, 3.0

of  $\text{Cl}^-$ , 2.8 of  $\text{Br}^-$  and 2.5 of  $\text{I}^-$  coinciding with Pauling's values with the choice (5). The concept can be extended to other ligands; thus  $x_{\text{opt}} = 3.5$  for  $\text{H}_2\text{O}$ , around 3.2 for most other oxygen-containing ligands including the somewhat indefinite value for oxide, 3.3 for  $\text{NH}_3$  but 2.8 for  $\text{N}_3^-$  and around 2.7 for sulphur-containing ligands [64]. The variation of  $x_{\text{opt}}$  as a function of the central atom is extremely regular; under equal circumstances, it decreases  $3d > 4d > 5d$ , it increases  $\text{M(II)} \ll \text{M(III)} < \text{M(IV)} < \text{M(V)} < \text{M(VI)}$ , and it increases linearly with the number of  $d$ -electrons (or with the atomic number, if one prefers) in a sequence of M having a constant oxidation state in a definite  $d$ -group [2]. The topic of electron transfer spectra has been reviewed recently [65].

Tetrahedral tetroxo complexes  $\text{MO}_4^{z-8}$  [51, 66] and tetrahalides  $\text{MX}_4^{z-4}$  [67, 68] also show conspicuous electron transfer spectra from which optical electronegativities of the central ions can be derived. It has sometimes been a difficulty that the  $d^a$ -transitions can be nearly as intense as electron transfer bands because of the lack of a centre of inversion. Surprisingly enough, the  $3d^5$  transitions of  $\text{FeX}_4^-$  and  $3d^7$  of  $\text{CoX}_4^-$  do not suggest that the complexes possess the full symmetry  $T_d$  [39] but rather show small deviations (due to  $l$ -mixing?) on an instantaneous picture. Post-transition-group  $d^{10}$  complexes, both octahedral  $\text{Sn(IV)}$ ,  $\text{Sb(V)}$  and  $\text{Pb(IV)}$  [57, 69] and tetrahedral  $\text{Hg(II)}$  and  $\text{Tl(III)}$  [70] halide complexes show electron transfer from filled M.O. mainly situated on the ligands to the empty  $s$ -orbital mainly localized on the central atom. However, in such cases, no sharp distinction can be drawn from Rydberg transitions to an extended orbital with no angular nodes such as known from  $\text{CBr}_4$ . A further complication occurs in alkyl iodides such as  $\text{CH}_3\text{I}$  where an electron transfer band (broad and weak) from  $5p$  to the  $3s$ -like Rydberg orbital centered around the adjacent carbon atom occurs at a lower wavenumber than the internal  $5p \rightarrow 6s$  excitation of the iodine atom [39]. When studying tetrahedral  $\text{ZnX}_4^-$ , Bird and Day [71] detected very strong absorption bands which may either be Rydberg transitions or, more probably, internal  $p \rightarrow s$  excitation of the halide ligands. Similar effects are observed [72] in  $\text{PtBr}_6^{2-}$  and  $\text{PtI}_6^{2-}$ .

Quadratic  $d^8$  tetrahalides formed by  $\text{Pd(II)}$ ,  $\text{Pt(II)}$  and  $\text{Au(III)}$  have electron transfer transitions to the empty  $(x^2 - y^2)$  orbital remarkably similar to those of low-spin  $d^6$  hexahalides [17, 66]. There is little doubt that the quadratic  $5p^2$  system  $\text{ICl}_4^-$  has an electron transfer band at lower energy than the comparable  $\text{XeF}_4$  [39] showing that the difference between the oxidizing character of iodine (III) and xenon (IV) is smaller than the difference between the excitation energy of fluoride and chloride ligands.

Electron transfer bands of  $4f$ -group complexes were not studied systematically before bromides and dialkyl dithiocarbamates were measured in ethanolic solution [73]. The variation of the wavenumbers for a given ligand

$$4f^6 \text{Eu(III)} < 4f^{13} \text{Yb(III)} < 4f^5 \text{Sm(III)} < 4f^{12} \text{Tm(III)} < \dots \quad (6)$$

corresponds to be *uncorrected optical electronegativities*  $x_{\text{uncorr}}$  evaluated without corrections for phenomenological parameters of interelectronic repulsion and for relativistic effects. The similarity between  $4f^q$  and  $4f^{7+q}$  is mainly due to the spin-pairing energy (2). The series (6) is the same obtained for the *decreasing* standard oxidation potentials of the corresponding  $\text{M(II)}$  aqua ions. Mixed oxides containing  $4f$ -group  $\text{M(III)}$  [74] and  $\text{M(IV)}$  [62] also show distinct electron transfer bands. This is also true for the green ytterbium (III) cyclopentadienide  $\text{Yb}(\text{C}_5\text{H}_5)_3$  [75]. Hexahalide complexes can be studied in acetonitrile solution of the  $4f$  [76] and the  $5f$ -group [77]. The best known electron transfer band of a  $5f$ -complex is the transition

from a combination of oxide  $\pi$ -orbitals having odd parity to the empty  $5f$ -shell of the uranyl ion, linear  $\text{OUO}^{+2}$  [78]. The luminescence of this transition, showing an extended vibrational progression, attracted early attention and led to the somewhat accidental discovery of the radioactivity of uranium. The excited state lives for about a millisecond and has very spectacular photochemical properties; thus, it tends to knock off small fragments of organic molecules much in the same way as ionizing radiation. Quite recently [79], electron transfer bands have been observed of microgram quantities of californium (III) and einsteinium (III) bromide complexes in ethanol indicating a position just after and just before ytterbium (III) in series (6). It is known from tracer experiments that mendelevium ( $Z = 101$ ) and nobelium ( $Z = 102$ ) are readily reduced in aqueous solutions to  $\text{Md(II)}$  and  $\text{No(II)}$ . It is possible to discuss the behaviour of the five transition groups in terms of the slope of  $x_{\text{opt}}$  (or the standard oxidation potential) across a given transition group [80] and because of the higher  $\langle r \rangle$  for the partly filled shell in the  $5f$  group than in the  $4f$ -group, the oxidation states tend to get high in the beginning, around Pa and U, and low at the end. The general question of the choice of oxidation states by a given transition group element can be related to much spectroscopic evidence [2, 81].

When the ligands have low-lying empty M.O., *inverted electron transfer* transitions can be observed when the central atom is sufficiently reducing, having a low ionization energy. In actual practice, such transitions occur only in the case of conjugated organic ligands. Williams [82] demonstrated that red colours of iron (II) and orange copper (I) complexes of dipyrindyl, phenanthroline *etc.* are due to such inverted transfer. The  $3d$ -group acetylacetonates [83] can be described by a theory where both normal (having  $x_{\text{opt}} = 2.7$  for the ligand) and inverted electron transfer bands occur. Many other organic ligands are in the same situation [54]. However it may be noted that non-conjugated  $\sigma$ -bonded organic ligands such as alkyl and phenyl groups, like hydride, do not produce normal electron transfer bands before an unusually high wavenumber, and that inverted electron transfer has not been observed with the possible exception of  $\text{M}(\text{C}_6\text{H}_5)_3$  ( $\text{M} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) having a lone-pair and a broad band in the ultra-violet [84]. This question is connected with the empty  $d$ -orbitals of M conceivably being involved in chemical bonding. On the whole, the spectroscopic evidence is against such valence-shell expansion [84].

Electron transfer bands can be recognized when the oxidation number of the central atom is well-defined [2]. If the oxidation number decreases by one unit in the excited state, we have normal electron transfer, and if it increases one unit, we have inverted electron transfer. We have discussed the various excitations roughly in the order of increasing tendency toward delocalization. All  $f^q$  and those of the  $d^q$ -transitions which are intra-sub-shell transitions produce narrow absorption bands. This is also possible outside the transition groups; thus, the blue colour of liquid oxygen [85] is due to narrow bands produced by the simultaneous (spin-forbidden  $S = 1 \rightarrow 0$ ) intra-sub-shell transitions in two adjacent  $\text{O}_2$  molecules. The inter-sub-shell  $d^q$  and  $p^q$  transitions, and the various  $l \rightarrow l'$  transitions such as  $4f \rightarrow 5d$ ,  $5f \rightarrow 6d$ ,  $5s \rightarrow 5p$ ,  $6s \rightarrow 6p$  and  $5p \rightarrow 6s$  all leave the oxidation state of the central atom unchanged. On the other hand, the genuine electron transfer transitions do not have even a remote analogy in atomic spectroscopy.

In chapter 3, we return to the situation of electron transfer between relatively distant atoms in solids and liquids. We may just mention that the excitation energies observed as electron transfer bands do not necessarily correspond to ionization energy differences between M and X because of eq. (4). Actually, it is quite conceivable that the ionization energy of the  $d$ -like orbitals in  $\text{FeBr}_4^-$  or  $\text{OsI}_6^-$

is larger than of the loosest bound M.O. mainly situated on the reducing ligands, since  $J(b, b)$  may be considerably larger than  $J(a, b)$ . The  $4f$ -shell of  $\text{Yb}(\text{C}_5\text{H}_5)_3$  almost certainly has a larger ionization energy than the loosest bound linear combination of cyclopentadienide orbitals which seems particularly influenced by inter-ligand anti-bonding [75]. Unfortunately, very little solid-state photo-electron spectroscopy of transition group compounds has been reported at a so relatively low energy as to include ionization of the partly filled shell, and only a few gaseous compounds such as vapours of  $\text{WF}_6$  [65] and  $\text{Fc}(\text{C}_5\text{H}_5)_2$  [6] have been studied by photo-electron spectroscopy.

### 3. ELECTRON TRANSFER BETWEEN DISTANT ATOMS AND COLLECTIVE EFFECTS

It has been recognized that anomalous long distance between a reducing and an oxidizing atom increases the wavenumber of the electron transfer band, presumably via the mechanism (4) where  $J(b, b)$  remains as an essentially intra-atomic quantity (1) when  $J(a, b)$  vanishes. At the same time, the intensity decreases dramatically because the square of the electric dipole moment of the transition vanishes if the « squared overlap »  $\int \psi_a^2 \psi_b^2 d\tau$  is zero, i.e. that the two orbitals  $a$  and  $b$  co-exist nowhere in our three-dimensional space. Thus, Linhard studied ion-pairs between cobalt (III) complexes such as  $\text{Co}(\text{NH}_3)_6^{+3}$  and iodide and found a weak, broad electron transfer band at about 10 kK higher wavenumber than of the complex  $\text{Co}(\text{NH}_3)_6\text{I}^{+2}$ . The concept of *anisotropic complexes* has also been introduced based on the existence of uranyl complexes  $\text{UO}_2\text{X}_N^{+2-N}$  having unusually long  $\text{U} - \text{X}$  distances in the equatorial plane and apparent optical electronegativities of  $\text{X}^-$  0.5 unit lower than normal. Some of the literature has been reviewed [39].

One may inquire into the consequences of a reducing and an oxidizing metallic element simultaneously being present in a compound. The colours of silver (I) salts are frequently unexpected; thus, yellow  $\text{CrO}_4^{2-}$  forms red  $\text{Ag}_2\text{CrO}_4$  and purple  $\text{MnO}_4^-$  blue  $\text{AgMnO}_4$ . The latter compound syncrystallized in colourless  $\text{AgReO}_4$  [60] has a new, broad band in the red which can be ascribed to  $\text{Ag}(4d) \rightarrow \text{Mn}(3d)$  electron transfer. Delépine had also noted the peculiar fact that orange-brown  $\text{IrCl}_6^{2-}$  forms dark blue  $\text{Ag}_2\text{IrCl}_6$  and dark green  $\text{Tl}_2\text{IrCl}_6$  [86]. Whereas the colours of purple  $\text{K}_2\text{IrCl}_6$  and brick-red  $\text{Cs}_2\text{IrCl}_6$  are caused by a moderate shift toward lower wavenumbers of the usual electron transfer bands of the anion, the unusual colours of the silver (I) and thallium (I) salts are due to a new, broad band at lower wavenumber (to the extent of some 5 kK) as is also true for salts of  $\text{OsX}_6^{2-}$  and  $\text{ReX}_6^{2-}$  [60].

From a chemical point of view, it may seem surprising that  $\text{Ag}(4d) \rightarrow \text{M}(5d)$  and  $\text{Tl}(6s) \rightarrow \text{M}(5d)$  should be among the best known cases of electron transfer between atoms of two metallic elements because many cations are far more reducing than  $\text{Ag}^+$  and  $\text{Tl}^+$ . However, this may be an effect of Franck and Condon's principle combined with the fact that most cations are protected by a layer of strongly coordinated water molecules. Actually, it is not quite easy to see from where the oscillator strength comes, because the « squared overlap » would be expected to be rather small. The phenomenon that  $\text{X} = \text{Br}$  pushes the wavenumber of the new band down by some 6 kK compared with  $\text{X} = \text{Cl}$  and hence, that it accompanies the normal electron transfer bands of  $\text{MX}_6^{2-}$ , might suggest that the  $4d$ -orbitals of the silver (I) or  $6s$ -orbital of thallium (I) get mixed up with the loosest bound M.O. of the anion. The same phenomenon is observed in the even stranger cases of antimony-doped

$A_2SnCl_6$  (becoming dark blue) and  $A_2SnBr_6$  (becoming dark red, in both cases having two new absorption bands) [87]. It is now known that individual entities  $SbX_6^{3-}$  and  $SbX_6^-$  having different Sb — X distances occur in these crystals, and the two new bands are undoubtedly due to electron transfer  $Sb^{III}Sb^V \rightarrow Sb^{IV}Sb^{IV}$  having two systems each with one 5s-like electron in the excited state. It is not quite easy to see why this state is not the groundstate, and one has to invoke the importance of adiabatically re-arranged internuclear distances and the « vertical » nature of the almost instantaneous excitation by the visible light in order to explain why the wavenumber is not zero. Such materials are said to be *electronically ordered*; the M.O. are not delocalized in such a way as to introduce serious doubt about the oxidation state of each individual antimony atom. Again, it is not easy to see from where the oscillator strength comes; the cubic crystal  $A_2MX_6$  has such a crystal structure that the shortest bridge between two M atoms goes through two consecutive X atoms [86]. It may be noted that the compound  $Sb^{III}Sb^VO_4$  contains crystallographically highly inequivalent Sb(III) and Sb(V); but this material is colourless.

The dark blue  $Ce_{1-x}U_xO_2$  crystallizing in the fluorite lattice like very pale yellow  $CeO_2$  and red-brown  $UO_2$  was originally [88] thought to involve an unusual situation of « valence oscillation » but it is more plausible [2] that this material is electronically ordered containing Ce(IV) and U(IV) in the groundstate and the  $U(5f) \rightarrow Ce(4f)$  transition producing the excited state Ce(III) and U(V). A comparable example, and one of the oldest known strongly coloured complexes, is Prussian blue  $KFe^{II}(CN)_6Fe^{III}$  having a cubic crystal structure containing equal amounts of low-spin ( $S = 0$ )  $Fe^{II}C_6$  and high-spin ( $S = 5/2$ )  $Fe^{III}N_6$  where the electron transfer  $Fe^{II}Fe^{III} \rightarrow Fe^{III}Fe^{II}$  produces the strong band, whereas purple  $KRu^{II}(CN)_6Fe^{III}$  shows the transition  $Ru^{II}Fe^{III} \rightarrow Ru^{III}Fe^{II}$  [89]. Similar electron transfer bands have been reported [90] of cobalt (II) and copper (II) hexacyanoferrates (II). The dark red colour of the uranyl compound  $K_2UO_2Fe(CN)_6$  must have a similar origin  $Fe^{II}U^{VI} \rightarrow Fe^{III}U^V$ . It is quite diagnostic that comparable hexacyanocobaltates (III) do not show such electron transfer bands. On the other hand, the thallium (I) hexacyanoferrate (III)  $Tl_3Fe(CN)_6$  is dark coloured because of  $Tl^IFe^{III} \rightarrow Tl^IFe^{II}$  in analogy to the salts of oxidizing hexahalide complex anions [91].

Robin and Day [92] have written an excellent review about the strong colours connected with *mixed oxidation states*. Most of these materials seem to be electronically ordered, though a few disordered cases such as  $Fe_3O_4$  are essentially black with very broad absorption both in the infra-red and the visible. It is a well-known fact from geology that most minerals and rocks are grey or black due to the simultaneous presence of iron (II) and iron (III). In a few cases, for instance in slightly oxidized vivianite (of which the stoichiometric form is  $Fe_3(PO_4)_2 \cdot 8H_2O$ ) bright blue colours are obtained. The finite wavenumber in the range 10 to 16 kK of the corresponding  $Fe^{II}Fe^{III} \rightarrow Fe^{III}Fe^{II}$  electron transfer band originates in the crystallographic non-equivalence, if by no other reason, by shorter  $Fe^{III}O$  than  $Fe^{II}O$  distances. Many  $Pt^{II}Pt^{IV}$  and  $Au^IAu^{III}$  compounds are strongly coloured for similar reasons, and it is quite characteristic that such absorption bands frequently are highly dichroic in polarized light. Apparently, black  $Pr^{II}Pr^{IV}$  and  $Eu^{II}Eu^{III}$  compounds involving mixed oxidation states are formed by the lanthanides, again raising the somewhat embarrassing question of the origin of the oscillator strength.

It should not be neglected that stoichiometric compounds in a few cases are known to have strong absorption bands which can only be ascribed to *collective effects*. Thus, Clark [93] made a careful study of the reflection spectra of many *d*-group halides, both binary  $MCl_2$  and double salts  $A_xMCl_{x+2}$ . In most cases, Clark

confirmed previous findings [94] that terminal and bridging halide ligands have almost the same spectrochemical effects. Thus, the perovskites  $\text{RbNiCl}_3$ ,  $\text{CsNiCl}_3$ ,  $\text{N}(\text{CH}_3)_4\text{NiCl}_3$  and the anhydrous  $\text{NiCl}_2$  have all the absorption spectrum characterizing the octahedral chromophore  $\text{Ni}(\text{II})\text{Cl}_6$  and showing only a minor variation of the sub-shell energy difference  $\Delta$ . However, anhydrous  $\text{TiCl}_3$ ,  $\text{TiBr}_3$  and  $\text{ZrCl}_3$  have very strong absorption in the visible, which can best be described as an excitation of the  $3d$  electron to a highly delocalized « conduction band ». It is interesting to compare with the dark violet titanium (III) tris (acetylacetonate) having an inverted electron transfer band [83].

The question of electron transfer between *identical* and equivalent atoms reminds one about Pauling's description of lithium metal as a resonance involving  $\text{Li}^+\text{Li}^-$  and  $\text{Li}^-\text{Li}^+$ . Actually, if a hypothetical crystal (like  $\text{Li}^+\text{H}^-$ ) is assumed to consist of  $\text{Li}^+\text{Li}^-$  it has a calculated heat of formation not much less negative than that observed for lithium metal. A comparable situation occurs with iodine molecules having a low-lying empty M.O. and their adducts with molecules having low or moderate ionization energy. Such « charge transfer » complexes are known both in solids, in liquid solution and in the gaseous state, and they have a quite characteristic electron transfer band. However, even the solution of iodine alone in carbon tetrachloride also shows such a band at 34.1 kK which does not follow Beer's law but has a molar extinction coefficient proportional to the iodine concentration [95]. A consistent explanation is that this band is due to the electron transfer from one constituent of a loosely bound dimer  $(\text{I}_2)_2$  to the other. Under these circumstances, it is not difficult to understand why crystalline iodine is suspected for disproportionating to a small extent into  $\text{I}^+\text{I}_3^-$  and other species supporting the observed electric conductivity.

This type of collective effect may be described as metallicity in the excited state. However, one should not apply the energy band model without a certain critical sense. There is more between Heaven and Earth than the solid-state physicists dream about, and it would be useful if some chemical argumentation might penetrate this type of discussion. It may also be worth attracting the attention to the *imaginary part* of the complex index of refraction. This imaginary part is inversely proportional to the average length of penetration of monochromatic light with a given wavenumber, and it is hence proportional to the sum of the molar extinction coefficients of the species present multiplied by their concentration in moles/litre. Since many solids have high molar concentrations, this imaginary part can become quite large and produce spectacular effects of highly anisotropic, and even metal-like specular, reflection in the strong absorption bands. It is emphasized that crystallinity is no condition for this effect; liquid bromine has a green metallic reflectance.

Indirect collective effects are, for instance, the green colour of Magnus' green salt  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  where the constituents are a colourless cation and a strawberry-pink anion. However, Day, Orchard, Thomson and Williams [96] gave convincing arguments that the  $5d^8$  transitions of the anion simply were shifted toward lower wavenumbers, and that the intense colour is due to high molar concentration in the solid and somewhat increased molar extinction coefficient. Anex *et al.* [97] found an intense band in the ultra-violet which is comparable to the very intense band of solid salts of  $\text{Pd}(\text{CN})_4^{2-}$  and  $\text{Pt}(\text{CN})_4^{2-}$  which has been extensively studied by many authors, especially in Liège and in Paris. The luminescence in the visible from this excited state depends much on a minor variation of the conditions, such as the nature of the cation or the number of water molecules of hydration per unit

cell. A major constituent of the excited orbital seems to be  $5p(z)$  or  $6p(z)$  orbital perpendicular on the plane of the tetracyanide anion.

With the exception of compounds showing such large-scale deviations from the principle of additivity of ionic colours, the collective effects are usually very weak in  $d$ - and  $f$ -group compounds. However, spin-forbidden transitions tend to intensify if the concentration of a  $d$ -group ion in a mixed crystal is increased. Thus, Lohr and McClure [98] pointed out that the  $3d^5$  transitions  $S = 5/2 \rightarrow 3/2$  in manganese (II) compounds are far weaker in the case of isolated chromophores  $\text{Mn(II)}\text{X}_6$  than in the case of bridged structures  $\text{MnXMn}$ . The  $3d^8$  transitions  $S = 1 \rightarrow 0$  in nickel (II) intensify as a function of increasing  $x$  in the mixed crystal  $\text{Mg}_{1-x}\text{Ni}_x\text{O}$  [99]. However, when the Néel temperature, the higher limit of anti-ferromagnetic behaviour, is passed for a given value of  $x$ , no spectacular spectral effects are observed. It is not even true for undiluted NiO that it has a particularly pronounced nephelauxetic effect, such as is the case for green  $\text{Cr}_2\text{O}_3$  compared with the red ruby [18, 100]. Only extremely subtle spectroscopic changes accompany the anti-ferromagnetic coupling [5, 101] though they have been detected in pairs of Mn(II) in ZnS [102].

A distinct, but rarely detected, collective effect is *simultaneous excitation* by one photon of two adjacent systems. This should not be confused with the recently discovered non-linear optical effect (in very high light intensities) of two photons inducing one excitation. Linz and Newnham [103] pointed out that CrOcr pairs in ruby have a set of narrow absorption bands in the ultra-violet which can be ascribed to simultaneous intra-sub-shell spin-forbidden transitions  $S = 3/2 \rightarrow 1/2$  as also known [104] from the highly anti-ferromagnetic blue « basic rhodo » complex  $(\text{NH}_3)_5\text{CrOcr}(\text{NH}_3)_5^{+4}$  and in a variety of other bridged  $\text{X}_5\text{CrOcrX}_5$ . From a quantum-mechanical point of view [5], this phenomenon can be understood by the simultaneous excitation not being spin-forbidden in the *total* system having  $S = 0, 1, 2, 3$  of the groundstate at slightly different energy. However, this argument cannot remove spin-forbiddleness by sheer magic; it is necessary that a non-negligible interaction occurs between the two sub-systems. We have already mentioned the interaction between two  $\text{O}_2$  molecules in liquid oxygen [85].

Another interesting aspect of the weakness of long-range interactions when studied by visible spectroscopy of the solid state is the rare observation of *co-excited vibrations of distant molecules*. Piper and Koertge [105] demonstrated the weak co-excitation of the O — H stretching frequency in  $\text{Ni}(\text{H}_2\text{O})_6^{+2}$  by deuterium substitution; and C — H and O — H frequencies are co-excited with a narrow intra-sub-shell transition in  $\text{OsCl}_6^{-2}$  in various solvents [106]. However, these co-excited vibrations are extremely weak in both cases. Regarding the general question under which circumstances vibrational structure belonging to M — X frequencies (usually the totally symmetric stretching normal mode) can be detected, it is quite frequent in intra-sub-shell transitions, e.g. in  $\text{ReCl}_6^{-2}$  [107] and  $\text{OsCl}_6^{-2}$  [106] as well as in solid chromium (III) compounds [14] and in the isoelectronic  $\text{MnF}_6^{-2}$  [108]. It is much rarer, even by cooling, in inter-sub-shell transitions. The electron transfer band of uranyl complexes shows clear-cut vibrational structure, like many of the electron transfer bands of tetroxo complexes [51]. It is favoured in the case of oxide and fluoride ligands because of the higher force constant and low ligand mass increasing the stretching frequency. Apparently, some  $3d^1$  transitions in vanadyl complexes show beginning vibrational structure, and it is present beyond doubt in the first spin-allowed  $3d^6$  transition of the red low-spin  $\text{NiF}_6^{-2}$  recently shown [109, 110] to have the spectrum predicted ten years before [108]. In the rather special case of octahedral 4/-hexahalides, the purely electronic transitions are almost absent [76] and one

observes only the co-excitation of one quantum of one of the three odd normal modes of vibration. This is also true for  $\text{UCl}_6^{-2}$  and  $\text{UBr}_6^{-2}$  [111].

Very few transition group compounds are sufficiently volatile for having had their spectra measured in the gaseous state, with exception of neutral hexafluorides such as  $\text{IrF}_6$ . De Kock and Gruen [112] studied gaseous, linear  $3d$ -group dihalides  $\text{XMX}$  having both characteristic  $d^d$  and electron transfer transitions with vibrational structure. Interestingly enough, the visible and ultra-violet absorption spectra are almost the same [113] when the triatomic molecules are trapped in cool matrices such as solid argon. Diatomic monoxides and monohalides  $\text{MX}$  have somewhat less chemical interest; the groundstate and many of the lower excited states belong to M.O. configurations of the  $3d^a-4s$  or  $3d^a-24s^2$  type like the neutral M atoms [114]. The M.O. description of diatomic molecules has been further reviewed [2, 39].

Going in the direction of simpler species, isolated atoms have been much studied in cool matrices. The easiest atoms to handle are xenon showing  $5p^6 \rightarrow 5p^56s$  and  $5p^55d$  transitions and mercury atoms showing  $6s^2 \rightarrow 6s6p$  transitions [2] but also alkali metal, manganese and several other atoms can be studied.

Returning to more normal states of condensed matter, the question of *approximate additivity of electric polarizabilities* in solid compounds and aqueous solution has attracted much attention recently [115, 116, 117]. This problem has the entirely practical connection with solid-state spectroscopy that the (real) index of refraction is directly connected with the molar concentrations and polarizabilities. Further on, it is a quite interesting theoretical subject because it is connected with the huge amount of oscillator strength concentrated in the far ultra-violet and soft X-ray region.

#### CONCLUSIONS

This paper is to a certain extent tertiary literature in the sense that it is a review of reviews. The various types of excitation of solid samples are a very heterogeneous collection, going from phenomena almost belonging to atomic spectroscopy such as the narrow absorption bands of  $4f$ -group compounds over the spectra of  $d$ -group complexes treated by ligand field theory and the angular overlap model and then to  $l \rightarrow l'$  inter-shell transitions and normal and inverted electron transfer bands, finally arriving at collective effects characterizing almost metallic bonding. It has only been possible to allow a small space to each relevant subject, and for instance, the organic « charge transfer complexes » consisting of organic molecules with a low ionization energy and of molecules such as  $\text{I}_2$ ,  $\text{TiCl}_4$ , tetracyanoethylene, etc. having a low-lying empty M.O. with relatively high electron affinity have not been treated. Strong chemical bonding is not always absent in apparent « charge transfer complexes »; thus  $\text{Fe}(\text{C}_5\text{H}_5)_2$ ,  $\text{C}_2(\text{CN})_4$  definitely is a molecular adduct with an electron transfer band at 10 kK [118] and the *groundstate* is not a ferricinium  $\text{Fe}(\text{C}_5\text{H}_5)_2^+$  salt of the anion  $\text{C}_2(\text{CN})_4^-$  though the latter anion can be formed in solution with mild reducing agents [119]. Actually, the crystallography of the platinum complex  $\text{Pt}[\text{C}_2(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3]_2$  is so complicated [120] that one may discuss [2] whether it is a three-membered ring involving a platinum (II) complex of bidentate  $\text{C}_2(\text{CN})_4^{-2}$  or whether the central C — C bond has been stretched so much that the complex has two unidentate  $\text{C}(\text{CN})_2^-$  ligands. Anyhow, it is not a typical olefin-complex like Zeise's anion  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  because the four CN groups are no longer coplanar with the central CC.

It has been argued by many authors that the electron transfer spectra are far less understood today than internal  $d^a$  or  $f^a$  transitions. However, this is much less so for well-characterized classes of complexes such as the hexahalides [65] where the group-theoretical arguments appropriate for octahedral symmetry can be applied. Actually, the electron transfer bands are perhaps of greater interest to the *chemist* than other transitions because they give a quantitative measure of how oxidizing is the central atom and how reducing the ligands on an instantaneous time-scale, following Franck and Condon's principle. The mononuclear complexes with only one central atom have been studied quite completely, at least as far as inorganic ligands go, but a fertile area for future work seems to be electron transfer between relatively distant atoms of metallic elements, such as the silver (I) and thallium (I) salts of oxidizing complex anions, as discussed here, or the cyanide complexes of two different elements. A special case is the colours of mixed oxidation states of the same element where the finite wavenumber of the transition is due exclusively to different internuclear distances. It is rarely the case that « something is wrong » with the groundstate of such systems; most frequently, both the excited and the ground levels have a well-defined [2] but differing distribution of oxidation states as exemplified by  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}} \rightarrow \text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$  and  $\text{Sb}^{\text{III}}\text{Sb}^{\text{V}} \rightarrow \text{Sb}^{\text{IV}}\text{Sb}^{\text{IV}}$  transitions.

As a personal remark, the writer may add that when he was first invited to drink tea in Professor Jannik Bjerrum's laboratory in Copenhagen, in 1950, literally *nothing* was known about the origin of the fact that most transition-group compounds are coloured. Only a few excited levels of lanthanides were identified, and there was not even a bad theory available for the  $d$ -groups. The evolution of this subject the last twenty years has almost exclusively been induction from experimental data and group-theoretical engineering, whereas attempts to quantum-mechanical calculations have been remarkably ineffective. This situation is analogous to the development of atomic spectroscopy between 1920-30. The electron configurations *classify* correctly the symmetry types and approximate order of energy of the *manifold* consisting of the groundstate and the discrete excited levels [2]. This is why one cannot « ameliorate » the wave-function of the groundstate of the helium atom by allowing two different radial functions (say, corresponding to the Slater exponents 1.1875 and 2.1832 rather than the conventional value 1.6875) without losing the advantage that all the excited levels known can be described by one-electron substitution in the preponderant configurations  $(1s)^1(nl)^1$ . This, and the unsatisfactory behaviour of M.O. configurations for large internuclear distances, are the main reasons why the energy band description is of very little use in non-metallic crystals. The excitations studied by visible and ultra-violet spectroscopy, as well as by X-ray and photo-electron techniques, are localized far more frequently than assumed by somebody believing in the energy band model. It is true that a closed-shell antisymmetrized total wave-function allows the individual orbitals to be re-written according to an arbitrary unitary transformation. The only trouble for this argument is that the true wave-function *is not* a well-defined configuration in the sense of one Slater determinant. The choice of the most suitable basis of orbitals (colloquially speaking being the eigen-functions of a Hartree potential) in the preponderant electron configuration is the art of quantum-chemical taxonomy. Knowledge of botany, Byzantine theology, and realizing the short average half-life of scientific theories, can be an excellent preparation for the spectroscopist walking unprotected into this no-man's land between physics and chemistry.

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