The dashed line in Figure 3 is the zero-order distribution function determined by hard-sphere packing, and the solid line is the first-order result. It is basically the attractive potential which produces the rounding of the peak; the effect of the softness of the repulsive potential is apparent only for $R < 1.03\sigma$, where $g(R)$ has fallen to about 1.5.

A more detailed comparison for the region of the first peak is shown for three thermodynamic states in Figure 4. In this case the solid line is our first-order result while the dashed line represents results calculated from the PY equation. It is clear that at low temperatures the BH theory gives a considerably more accurate radial distribution function than does the PY theory.

Thus it appears that part of the success (relative to the PY theory) of our perturbation theory is due to the fact that our procedure for calculating thermodynamic properties is more similar to the energy method than to the pressure or compressibility methods but that part is also due to the fact that the perturbation theory gives a more accurate $g(R)$.

Other Perturbation Theories

Recently, two theories similar to the BH perturbation theory have been developed. The first is that of Mansoori and Canfield[28] and Rasaiah and Stell,[29] who show that the perturbation series of Zwanzig,[3] when truncated after first order, is an upper bound on A. They choose d to minimize this upper bound. This approach gives fairly good results at low temperatures, but the results become worse as the temperature is increased because the finite steepness of the repulsive portion of the potential has not been adequately treated.

Very recently, Weeks, Chandler, and Andersen[30] (WCA) have proposed an interesting perturbation theory which uses a reference fluid whose potential is

(28) G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.*, **51**, 4958 (1969).
(29) J. Rasaiah and G. Stell, *Mol. Phys.*, **18**, 249 (1970).
(30) J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, **54**, 5237 (1971).

given by eq 9, where R_m is the value of R for which

$$u_0(R) = u(R) + \epsilon \quad (R < R_m)$$
$$0 \quad (R > R_m) \tag{9}$$

$u(R)$ is a minimum. For the 12–6 potential $R_m = 2^{1/6}\sigma$.

The difficulty with the WCA theory is that the properties of their reference fluid are not well known. To overcome this, they introduce a number of untested approximations. As may be seen from Figure 4, they obtain very good results at high densities. In order to examine their theory, we have made some Monte Carlo studies of their reference fluid and have found that the RDF which they propose as an approximation to that of the reference fluid is actually a better approximation to that of the 12–6 fluid than to that of the reference fluid. This results from the use of the PY hard sphere RDF. If accurate values for this function are used their RDF approximates well that of the reference fluid but less closely that of the 12–6 fluid. Their approach is promising.

Summary

In this review we have briefly considered three treatments of the equilibrium properties of the liquid state: computer-simulation methods, the PY theory, and perturbation theory. The computer-simulation methods are exact treatments and provide valuable quasiexperimental data for model systems. However, they have the disadvantage of requiring large amounts of computing time and they often provide little intuitive insight. The PY theory requires moderate amounts of computing time and, if used with the energy equation, gives satisfactory results for the thermodynamic properties. However, it yields even less insight than do the simulation studies. On the other hand, the BH perturbation theory requires very little computing time, gives excellent results, and provides considerable insight into the factors determining the structure of liquids.

Persistence of Atomic Orbitals in Complexes and Other Compounds

CHRISTIAN KLIXBÜLL JØRGENSEN

Institut de Chimie Physique, Université de Genève, 1211 Geneva 4, Switzerland

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Orbitals are, strictly speaking, the wave functions of stationary states of systems containing one electron. From the point of view of quantum mechanics it is by no means obvious that atoms or monatomic ions containing more than one electron can be described in terms of *electron configurations* in which each electron is assigned to an orbital, with no more than two electrons in any orbital. Yet the "buildup" or Aufbau of the periodic table is based on this very picture. It is perhaps even more surprising that the ground state and the low-lying excited levels of molecules and polyatomic ions can be classified spectroscopically in terms of one-electron con-

figurations. Photoelectron and X-ray spectra of compounds clearly demonstrate the persistence of inner shell orbitals in a given element. The apparent persistence of one-electron orbitals in complex systems forms the main topic of this Account.

The underlying quantum-mechanical basis for the one-electron approach is placed in perspective particularly with regard to symmetry classifications of states in atoms, molecules, and polyatomic ions. For quantitative purposes the one-electron picture cannot succeed, and configuration interaction must be involved. Nevertheless, as shown below, the concept of a *preponderant electron configuration* with its one-electron picture is generally relevant and of immense value for qualitative considerations as well as for matters of symmetry classification.

Atoms and Monatomic Ions

First let us review the role of orbitals in the description of the elements. Mendeleev was firmly convinced that the periodic table had a more fundamental origin than the order of increasing atomic weights. Rydberg proposed in 1906 that the atomic spectra indicate a mathematically consistent structure based on integers; he suggested that the groups of elements each ending with a noble gas contain 2, 2, 8, 8, 18, 18, 32, 32, ..., $2n^2$, $2n^2$, ... elements, respectively. This conjecture turned out to be correct with the exception of the supposed elements nebulium and coronium assigned the numbers 3 and 4. Their spectral lines (which could not be reproduced in the laboratory) later turned out to be due to forbidden transitions in the oxygen ion, O^{2+}, and highly ionized iron, *e.g.*, Fe^{13+}, respectively.

It is not generally recognized that a minor uncertainty occurred when Moseley determined the atomic number, Z, from the energy levels

$$E = -(Z - \sigma_{nl})^2 \text{ ry}/n^2 \qquad (1)$$

where 1 ry = 1 rydberg unit = 109,737 cm^{-1} = 13.60 eV = 313.5 kcal/mole. The uncertainty arose because the screening constant, σ_{nl}, even in the most favorable case, nl = 1s, increases from 0.31 for helium to a value between 2 and 3.5 for heavier elements. Because of a relativistic effect, the screening constant decreases in very heavy elements and becomes negative for Z above 100. For n greater than 1, the screening constants are quite large, and eq 1 loses its physical significance entirely for penultimate orbitals.

From Rydberg's studies of alkali-metal atoms and isoelectronic ions such as Ca$^+$, another formula was derived for outer electrons

$$E = -(z + 1)^2 \text{ ry}/(n - \delta_l)^2 \qquad (2)$$

where z is the ionic charge of M^{z+} and the Rydberg defect, δ_l, is almost independent of n but a decreasing function of increasing l (and close to zero for l = 3 when Z is below 55, and for all known cases with l above 3). Both inner shell (eq 1) and outer shell electrons (eq 2) show relativistic effects (the first-order result is also called "spin–orbit coupling") where positive l values correspond to $j = l + \frac{1}{2}$ at higher energy and $j = l - \frac{1}{2}$ at lower energy. The energy difference between the two j values increases dramatically when l and n decrease. For inner shells, when Z is high, it may be many rydbergs.

Both the X-ray spectra described by eq 1 and the spectra of atoms in the visible and the near-ultraviolet regions which can be classified as the allowed transitions between the energy levels of eq 2 are effectively one-electron phenomena. Thus, eq 2 refers to one electron outside closed nl shells each containing $(4l + 2)$ electrons, whereas eq 1 refers to a single "hole" in a closed shell only containing $(4l + 1)$ electrons.

It is not at all clear what atomic orbitals *are* in the general case of many-electron systems. Around 1923, it was certain that Bohr's semiclassical model of the hydrogen atom proposed 10 years earlier could not be extended to atoms containing more than one electron. On the other hand, it turned out that quantum numbers could be assigned to each energy level in such a way as to be compatible with a certain set of rules first proposed by Hund. We return to the Schrödinger interpretation of these rules below, but the important point here is the feasibility of a classification where one or several energy levels belong to a definite electron configuration, in which each nl shell is assumed to contain 0, 1, 2, ..., $(4l + 2)$ electrons. The ground state of the neutral atom has most frequently the electron configuration obtained by consecutive filling of the shells

1s $\ll$ 2s < 2p $\ll$ 3s < 3p $\ll$ 4s < 3d < 4p $\ll$ 5s < 4d <
$\qquad$ 5p $\ll$ 6s < 4f < 5d < 6p $\ll$ 7s < 5f < 6d < .... (3)

where the double inequality signs indicate the noble gases containing 2, 10, 18, 36, 54, 86, 118, ... electrons. It is very important for chemists to note that the monatomic ions M^{2+}, M^{3+}, and M^{4+} fill their shells in the order

1s $\ll$ 2s < 2p $\ll$ 3s < 3p $\ll$ 3d < 4s < 4p $\ll$ 4d < 5s < 5p $\ll$
$\qquad$ 4f < 5d < 6s < 6p $\ll$ 5f < 6d < 7s < .... (4)

to which only four exceptions (La^{2+}, Gd^{2+}, Ac^{2+}, and Th^{2+}) are known. The double inequality signs indicate ions such as Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+} which are isoelectronic with the noble gases. Other closed-shell systems corresponding to chemically well-known species are Zn^{2+}, Cd^{2+}, Sn^{2+}, Yb^{2+}, Hg^{2+}, Pb^{2+}, and No^{2+} (Z = 102). The *compounds* of the five transition groups contain only *one partly filled shell*, either 3d, 4d, 4f, 5d, or 5f as determined by eq 4.

The One-Electron Problem. Let us examine the one-electron problem in the light of modern theory. As seen from the point of view of quantum mechanics, a given energy level, E, of a monatomic species has the well-defined quantum number J and either *even* or *odd* parity. If the energetic separation between the two j components of a positive l value is relatively small, the *Russell–Saunders coupling* is a good approximation, and closely adjacent J levels can be grouped together in *terms* having definite values of the quantum numbers of total spin (S) and orbital (L) angular momentum. *If* the wave function Ψ of the many-electron system be-

longs to a definite electron configuration, the parity is the (even or odd) value of the sum of all l values, and the possible values of J, S, and L can be found according to well-understood rules. In the particular case of only one partly filled shell $(nl)^q$ (traditionally, the number of electrons in an orbital or a set of degenerate, equivalent orbitals is written as a right-hand superscript) the configuration consists of $(4l + 2)!/[q!(4l + 2 - q)!]$ *states*, mutually orthogonal Ψ. Each energy level corresponds to $(2J + 1)$ states and each term to $(2S + 1)(2L + 1)$ states. Schrödinger's equation for the (negative) eigenvalues E for one electron having the wave function ψ can be written for a conservative electrostatic potential, $U(x,y,z)$ (chosen negative when electrons are stabilized), as eq 5, in atomic units (energy: 1

$$\mathcal{P}(x,y,z) + U(x,y,z) = E \tag{5}$$

hartree = 2 rydbergs; length: 1 bohr = 0.529 Å). The *kinetic pseudopotential* for real (noncomplex) ψ is given by eq 6. The local contribution $\mathcal{P}\psi^2$ to the kinetic en-

$$\mathcal{P} = -\frac{1}{2\psi}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] \tag{6}$$

ergy is negative in points with $U > E$. In the case of spherical symmetry where $U(r)$ depends only on the distance r from the origin (at which point the nucleus of an isolated atom can be situated), eq 7 is followed. The

$$\psi = A_l R_{nl}/(2\pi^{1/2}r) \tag{7}$$

angular function A_l is a normalized linear combination of homogeneous polynomials $x^a y^b z^c/r^l$ (with the nonnegative integers $a + b + c = l$). The kinetic pseudopotential

$$\mathcal{P} = \frac{l(l + 1)}{2r^2} - \frac{1}{2R_{nl}}\frac{\partial^2 R_{nl}}{\partial r^2} \tag{8}$$

consists of an angular part (vanishing for $l = 0$) and a radial part dependent on the radial function R_{nl}.

The Hartree approximation consists of finding one-electron functions (eq 7) which are eigenfunctions (eq 5) of a Hartree potential, $U(r)$, considered as the sum of the nuclear attraction, $-Z/r$, and the repulsion from the *other* electrons. If q electrons are present, $q(q - 1)/2$ contributions to the interelectronic repulsion have to be calculated. If $U(r)$ were approximately $-(Z - \sigma_{nl})/r$, eq 1 would be obtained. Since U decreases more rapidly than $-(z + 1)/r$ for small r, it can be argued that δ_l of eq 2 represents a certain cancellation by the potential energy of the angular part of eq 8 for positive l. The energy differences between various (S,L) terms belonging to the same electron configuration are due to slightly different average values of the reciprocal interelectronic distance $(1/r_{12})$ in the partly filled shell.

The tables compiled by Moore[1] clearly show that, by means of electron configurations, one can *classify* the J levels correctly. In most atoms, S and L are also fairly good quantum numbers. Complicated configura-

tions, such as $[Xe]4f^2$ and $[Xe]4f5d$ of Pr^{3+}, have a large number of predicted J levels which have been identified almost completely.[2]

Unfortunately, it is certain that the actual Ψ are not particularly well represented by pure configurations.[3] For quantitative considerations this is a serious matter. Whereas the electronic density in our three-dimensional space is close to the sum of ψ^2 (Hartree orbitals), the interelectronic repulsion is considerably smaller (the *correlation effect*) and the term distances within the same configuration are especially reduced. This inadequacy of well-defined configurations can be described in terms of nondiagonal elements, E_{12}, the energy of interaction of a given configuration with excited configurations E_2. If they are well separated from the ground configuration E_1, second-order perturbation theory predicts the stabilization $(E_{12})^2/(E_1 - E_2)$. The atomic spectroscopists hoped for a long time that such "configuration mixing" would only be of importance when two configurations of the same parity overlap or, at most, are separated by energies comparable to their own widths, such as is the case for $[Ar]3d^q4s^2$ and $[Ar]3d^{q+1}4s$ in neutral iron group atoms. Unfortunately, the nondiagonal elements E_{12} are the largest with *continuum configurations* having E_2 higher than the first ionization energy of the system. In general, excited configurations $a^2 \rightarrow b^2$ in which two electrons are promoted from the original configuration produce the largest nondiagonal elements, E_{12}. The most effective continuum orbitals b for this purpose have almost the same average r as the original a, and are sometimes called *deformation orbitals* or *polarization orbitals*.

In order to explain the major part of the correlation effect, it is necessary to take into account at least twice as many b orbitals as the original a orbitals, resulting in extremely lengthy calculations approaching the practical limit for more than ten electrons. Though there is a risk that the word may enter textbooks and science fiction, one may think about these continuum effects as an *internal dielectric constant* diminishing the interelectronic repulsion.

It is evident that the concept of atomic orbitals cannot be clear-cut in monatomic species containing two or more electrons. Usually, a major contribution to the total wave function Ψ consists of the definite configuration used for the classification,[1] and it can be argued that it is always possible to make a valid distinction between this major component and all other, minor components. However, the definition[4] of the *preponderant electron configuration* is the more fundamental property: it is possible to predict the symmetry types (J, parity, S, and L) of the excited levels (in atoms frequently 20 to 400 such levels[1]) by replacement of one, two, or three electrons in the ground configuration with electrons in definite nl orbitals. When the lowest configuration

(1) C. E. Moore, *Nat. Bur. Stand. (U. S.) Circ.*, **No. 467** (1949, 1952, 1958).

(2) J. Sugar, *J. Opt. Soc. Amer.*, **55**, 1058 (1965).

(3) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

(4) C. K. Jørgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, West Berlin and Heidelberg, 1969.

contains partly filled shells, several excited levels in addition to the ground state are correctly classified by the same configuration. It was not obvious that such a classification based on the preponderant electron configuration would work at all, and it may be[4] that its success has something to do with Bertrand Russell's theory of higher types involving properties of classes as distinct from the properties of the individual members.

Orbitals in Molecules. Since the time of Hund and Mulliken, the one-electron picture or orbital view has been extended to molecules. The ground state and the excited states of molecules are described by configurations of molecular orbitals (MO). In the approximation of Russell–Saunders coupling, these configurations or energy levels are classifiable according to electron spin and orbital angular momentum. The symmetry types are S and Λ for diatomics and other linear molecules and S and Γ_n for nonlinear, polyatomic molecules. If the nuclear skeleton possesses a center of inversion, even (g = gerade) or odd (u = ungerade) parity is added to the symmetry type. Correspondingly, the individual MO's themselves are one-electron wave functions, ψ, having definite λ (the values 0, 1, and 2 are called σ, π, and δ) or γ_n. In systems having a center of inversion, $\psi(x,y,z) = -\psi(-x,-y,-z)$ for ψ_u, whereas ψ_g do not change when all three coordinates change sign. The MO's are the solutions to Schrödinger's equation (eq 5) for a Hartree potential, $U(x,y,z)$, having the same symmetry as the point group of the nuclear skeleton of the species. Accordingly, the linear symmetries have U only depending on z and ρ (where $\rho^2 = x^2 + y^2$) and, in the case of $D_{\infty h}$ having a center of inversion, $U(\rho,z) = U(\rho,-z)$.

The MO configurations are "preponderant" in the same sense[4] as in atoms so that some correlation effects (mixing with other configurations differing in ψ for two electrons) are inevitable. However, a more serious problem is that Ψ for a polyatomic entity also depends on the positions of the nuclei, and the *local site symmetry* is the appropriate point group to use only in such cases where the internuclear distances are moderately short. Thus, at the equilibrium distance ($R = 0.75$ Å in the hydrogen molecule) the ground state has the preponderant configuration $(\sigma_g)^2$, like $(1s)^2$ of helium. When R increases beyond 2 Å, this becomes a very bad approximation. For large R, Ψ is a mixture of equal portions of $(\sigma_g)^2$ and $(\sigma_u)^2$, and it is well described as two individual hydrogen atoms each having the configuration (1s).

In large molecules, it is imperative to make a distinction between *relevant* and *irrelevant* symmetry components.[3] Frequently, it is not only a good approximation to apply another point group than the one actually possessed by the nuclear skeleton, but a *better* approximation. One of the main problems of *applied group theory*[5,6] is to investigate the physical significance of the

phrase "The molecule MX_N *almost* has the symmetry G," though it may seem intuitively clear to the chemist. For the mathematician, the presence or absence of the point-group G is clear-cut. However, when more than one electron occurs in the system, the MO may be more or less successful in forming preponderant configurations in a way dependent on the G to which they are adapted. Furthermore, octahedral MX_6 may be very slightly deformed in such a way that the strict symmetry is a subgroup of O_h such as D_{4h} or D_3 or even the lowest subgroup, C_1, but the *relevant symmetry* may remain O_h if the deviations are small.

trans-$Cr(NH_3)_4F_2^+$ contains the *chromophore trans*-$Cr^{III}N_4F_2$ of symmetry D_{4h} (if the hydrogen atoms of each ammonia ligand are considered to be freely rotating in a circle). The reddish brown color is due to absorption bands corresponding to four excited levels. There would only have been two such bands in yellow $Cr(NH_3)_6^{3+}$ and green CrF_6^{3-} containing the chromophores $Cr^{III}N_6$ and $Cr^{III}F_6$, being regular octahedral O_h (the latter complex shows, in addition, rather prominent spin-forbidden transitions to excited levels with $S = 1/2$ from the ground state with $S = 3/2$). The interesting point is that the four excited levels with $S = 3/2$ of *trans*-$Cr^{III}N_4X_2$ (with various X) in two cases have strongly mixed MO configurations adapted to D_{4h} though they are well defined, in the preponderant sense, from the point of view of O_h symmetry. Hence, it is the operator of interelectronic repulsion which makes it necessary to accept the chemist's opinion that the complex is approximately octahedral.

Attempts to solve the problems related to relevant symmetry are made by the introduction of *generated symmetry*.[7] A simple case is the *holohedrized symmetry* $U[+C_i]$ where the average value $(U(x,y,z) + U(-x,-y,-z))/2$ is evaluated after the origin has been selected as a virtual center of inversion. The residual part of the Hartree potential, $U[-C_i] = U - U[+C_i] = (U(x,y,z) - U(-x,-y,-z))/2$, is called *hemihedrized*. The *catoptrized symmetry* $U[+C_s]$ is obtained by forming the average value $(U(x,y,z) + U(x,y,-z))/2$ after selection of a virtual plane of symmetry (mirror plane), $z = 0$. Whereas the eigenfunctions ψ in holohedric symmetries have even or odd parity, the ψ of C_s have the property "π" when $\psi(x,y,z) = -\psi(x,y,-z)$ and "σ" when they are invariant. Organic chemists and other people accustomed to planar molecules use the symbols "σ" and "π" without quotation marks, but it is running the risk of confusion with the symbols σ, π, δ, ... in linear symmetries indicating the degree λ of the homogeneous polynomials $x^a y^b / \rho^\lambda$ ($a + b = \lambda$).

The finite point groups of order N_G can be generated[7] by taking the average value of $U(x,y,z)$ in N_G different points. Thus, the group O_h is generated from 48 points, representing all combinations of the six permutations of x, y, and z with the eight positive and negative signs of the three coordinates. If only the 8 latter points are

(5) J. W. Leech and D. J. Newman, "How to Use Groups," Methuen, London, 1969.
(6) F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963.

(7) C. K. Jørgensen, "Modern Aspects of Ligand Field Theory," North-Holland Publishing Co., Amsterdam, 1971.

considered, the orthorhombic group D_{2h} is generated, and if x and y are then permuted, the 16 points generate $U[+D_{4h}]$. Both the cubic groups T_d and T_h and O are generated by three different choices of 24 points, and the icosahedral symmetry with center of inversion K_h can be generated from U in 120 points. The infinite point groups can be generated by integration, $U[+R_{3i}]$, by finding the average value of U on the spherical surface with given r; $U[+C_{\infty v}]$ can be generated by finding the average value of U on the circle with definite ρ and z; and $U[+D_{\infty h}]$ can be generated by subsequent holohedrization, $(U(\rho,z) + U(\rho,-z))/2$. It is fascinating[7] that only two of the five linear symmetries can be represented by a one-valued scalar function, $U(x,y,z)$. Flow diagrams of the type known from botanical identification are given[8,9] for easy determination of the point group of a given molecule.

When seeking approximate expressions for MO's, two rather different starting points are possible. It is conceivable to perform direct numerical calculations for molecules. For example, there is Hartree's technique for evaluating R_{nl} of eq 7 in many-electron atoms. In actual practice, this has only been done for a few diatomic species and in the case of crystalline materials where a unit cell is repeated infinitely. In strongly conducting metals, the loosest bound electrons have ψ which are essentially those of free electrons in a constant potential U, only modified in the relatively small volume of the atomic cores because ψ must remain orthogonal to all the previously filled orbitals. Various semiconducting crystals have been treated along these lines by the "augmented plane-wave method." However, other compounds are more readily described in the "tight-binding approach" corresponding to the *linear combination of atomic orbitals* (LCAO) in isolated molecules. We will consider this model with a small basis set with one or two AO energy values from each atom. If a large number of AO's is included in the basis set, it becomes much more flexible (in the limit of the "united atom" which is only applicable in practice to hydrogen compounds such as HX and CH_4, all the orbitals are centered around the same nucleus), and the choice of individual orbitals is without great physical importance but the computer time needed becomes very long. There is no evident reason why the MO should be very close to LCAO consisting of one or two shells from each atom.

One argument for LCAO might have been that the chemical bonding only has a very small influence on the total energy of the molecule. With the exception of H_2 (17% more stable than two H atoms), even strongly bound molecules have rather negligible effects, e.g., N_2 is only 0.3% more stable than two nitrogen atoms. However, this argument is to some extent an illusion. Unlike the case of nuclei, which have a rest-mass 0.8–0.9% lower than the constituent protons and neutrons, the electronic systems consist of particles (elec-

trons) situated in a variety of highly nonequivalent orbitals. The total binding energy is $-Z^{2.4}$ ry (according to Gombas), of which nearly $-2Z^2$ ry is connected with the two innermost (1s) electrons in eq 1. In thorium atoms, for example, this binding energy amounts to the rest-mass of 1.2 electrons, corresponding to 3 ppm of the total mass, whereas chemical binding energies correspond to changes in mass which are at most effects in the ninth (H_2) or tenth decimal place.

The most obvious modification of AO's in heteronuclear molecules is the adaptation to the fractional atomic charges δ, with the result of contracting the radial functions relative to neutral atoms for positive δ. The *nephelauxetic effect*[10,11] is the decrease of parameters of interelectronic repulsion for partly filled d and f shells in complexes compared with the corresponding gaseous ion M^{z+}. This effect is partly due to δ being smaller than z (though δ in most cases[4,12] seems to be larger than 1, in contrast to Pauling's electroneutrality principle). Partly it is due to delocalization on the ligands. Whereas the coefficients of LCAO in homonuclear molecules are determined largely by symmetry alone, the delocalization coefficients in typical complexes allow a continuous series of intermediate cases of partly covalent, partly ionic, bonding. A second important modification of AO pointed out by Ruedenberg[13] is that bonding MO's have intrinsically contracted radial functions (this has been verified by X-ray diffraction of hydrogen compounds), and antibonding MO, intrinsically expanded AO constituents.

Polyatomic Ions

Ligand Field Theory and the Angular Overlap Model. We turn next to an examination of polyatomic ions from the point of view of ligand field theory and the angular overlap model. In a fully ionic compound containing the central ion M^{z+}, the Hartree potential, $U(r)$, is changed by addition of the *Madelung potential*

$$V = -\sum \frac{q_k}{R_{ik}} = V_0(r) + V_{res}(x,y,z) \qquad (9)$$

being a summation over the charges q_k on the other atoms at the distance R_{ik} from the point i considered. There is no doubt that the spherically symmetric average value V_0 is of great importance for the bonding of highly electrovalent crystals such as NaCl, CaF_2, or ThO_2. Bethe suggested in 1929 that the nonspherical part, V_{res}, produces the five different orbital energies if the central ion contains a partly filled d shell or, correspondingly, seven slightly different energies of f orbitals. Though widely accepted by chemists after 1952, this is not at all a satisfactory model[14,15] for the "ligand

(8) M. Zelkin, *J. Chem. Educ.*, **43**, 17 (1966).
(9) J. Donohue, *ibid.*, **46**, 27 (1969).

(10) C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).
(11) C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962).
(12) C. K. Jørgensen, *Helv. Chim. Acta, Fasc. Extraord. Alfred Werner*, 131 (1967).
(13) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).
(14) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962.
(15) C. K. Jørgensen, *J. Phys. (Paris)*, **26**, 825 (1965).

field" effects. It was recognized around 1956 that the distinction between antibonding and nonbonding MO's, mainly consisting of central-atom l orbitals, is the only explanation possible. The fact that the higher subshells are antibonding MO's results in delocalization being more pronounced on *less* electronegative ligands and for higher oxidation states of the central atom.[4,12]

The 4f compounds have such weak "ligand field" effects that the J levels of spherical symmetry can be recognized. The very small energy differences between the seven 4f orbitals are only obtained after considerable mathematical manipulation, but they agree[16] with the expectation for weak antibonding effects. This description was extended to the *angular overlap model*[7,15,17-21] where the antibonding effects can be transferred from one chromophore to another with different symmetry or with different coordination number N. In particular, it can be shown[17] that the antibonding effect is the product of a quantity, expected to vary with the M-X distance R as R^{-5}, and the square A_i^2 of the central atom angular function (eq 7), summed over each position of the X nuclei. If only one l shell is considered, the energy levels (but not band intensities, etc.) depend *only* on the holohedrized symmetry of the chromophore. Thus, a regular tetrahedron (T_d) becomes a cube (O_h) after holohedrization, thus explaining the fact that fac-$Cr(CN)_3(H_2O)_3$ has exactly the spectrum[22] expected for an octahedral complex of a hypothetical ligand $(CN^- + H_2O)/2$. Though the symmetry of this complex is only C_{3v}, the holohedrized symmetry is O_h. On the other hand, NH_3 of symmetry C_{3v} has the holohedrized symmetry D_{3d}.

Orthoaxial chromophores[18] have all the ligand nuclei on Cartesian axes. Orthoaxiality is not at all a property of a given point group; an octahedron with six different ligands has the symmetry C_1 and may be orthoaxial, while cubal MX_8 (O_h) and icosahedral MX_{12} (K_h) are not orthoaxial. Orthoaxial chromophores have only three alternatives of holohedrized symmetry: O_h, D_{4h}, and D_{2h}. In other words, the residual $U[-D_{2h}]$ after generation of orthorhombic symmetry has no energetic effect. The division of the Hartree potential in components

$$U = U[+R_{3i}] + U[-R_{3i} + O_h] +$$
$$U[-O_h + D_{4h}] + U[-D_{4h} + D_{2h}] + \ldots \quad (10)$$

is rather similar to the division of the Madelung potential, V, of eq 9 in a spherical component, a (specifically) octahedral component, a (specifically) tetragonal component, and so on. The spherical component $U[+R_{3i}]$ determines the radial expansion of R_{nl} and the octa-

hedral component $U[-R_{3i} + O_h]$ the energy difference between the two subshells formed by two and three d orbitals (not as a pure potential perturbation $U\psi^2$ but *via* eq 5 and the condition of mutually orthogonal ψ_1 and ψ_2). It has been clear since 1955 that the subshell energy difference Δ (originally called $10Dq$) does not depend on whether the ligands are neutral or are anions. The arguments of Ruedenberg[13] can be extended to the hypothesis[7,23] that the phenomenological parameters of the angular overlap model are connected with the kinetic operator $\mathcal{P}$ of eq 6, increasing the local contribution $\mathcal{P}\psi^2$ in the *bond region* between M and X for antibonding MO. Continuing previous ideas of Hückel, Mulliken, Wolfsberg, and Helmholz, this effect is proportional to the square of the overlap integral between ψ_M and ψ_X in the asymptotic limit of *weak* covalent bonding. Hence, it is the need for orthogonalization of the partly filled shell on the occupied ligand orbitals which produces the "ligand field" repulsion.

Mixing of l Values and the Gillespie Effect. Useful one-electron orbitals can be fashioned by the superposition of AO's having different orbital momenta, l. (This is often called "hybridization" with considerable ambiguity in some cases.) It is an experimental fact that many molecules and polyatomic ions do not achieve the highest possible symmetry available to the nuclear skeleton. Thus, NH_3, PH_3, PF_3, SO_3^{2-}, ClO_3^-, $SnCl_3^-$, $SbCl_3$, $TeCl_3^+$, IO_3^-, and XeO_3 are pyramidal (C_{3v}) and not planar (D_{3h}). The oxidation states[4] phosphorus(III), sulfur(IV), chlorine(V), tin(II), antimony(III), tellurium(IV), iodine(V), and xenon(VI) correspond to closed-shell gaseous ions M^{z+} having two electrons in the loosest bound s orbital. Orgel[24] pointed out that the *lone pair* of such complexes is a mixture of s and p character. Since the lone-pair MO no longer has well-defined parity, and the electronic density ψ^2 no longer has even parity, the lone pair is able to concentrate on the side of the central atom opposite to the ligands. Expanding previous ideas of Lewis and Sidgwick, Gillespie[25] suggested that lone pairs need the same or somewhat larger angular space than ligands, and that pyramidal MX_3 with one lone pair really are tetrahedral, like the resolution of $RR'R''S^+$ or $RR'SO$ in optically active forms shows. Pearson[26] pointed out that this l mixing is the same as a second-order Jahn-Teller effect (vibronic mixing with excited electronic levels of opposite parity) which may be static (in the equilibrium internuclear distances) or dynamic (only modifying the vibronic wave functions). The problem is rather complicated[27,28] because crystallographic studies may indicate a time-average structure of high symmetry (like ammonia at high temperatue showing no pronounced deviation from planarity), whereas visible and ultraviolet absorption spectra indicate an almost instan-

(16) C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, *J. Chem. Phys.*, **39**, 1422 (1963).
(17) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).
(18) C. E. Schäffer and C. K. Jørgensen, *Kgl. Dan. Vidensk. Selsk., Mat.-fys. Medd.*, **34**, No. 13 (1965).
(19) C. E. Schäffer, *Proc. Roy. Soc. (London)*, A297, 96 (1967).
(20) C. E. Schäffer, *Struct. Bonding (Berlin)*, **5**, 68 (1968).
(21) C. E. Schäffer, *Pure Appl. Chem.*, **24**, 361 (1970).
(22) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

(23) C. K. Jørgensen, *Chem. Phys. Lett.*, **1**, 11 (1967).
(24) L. E. Orgel, *J. Chem. Soc.*, 3815 (1959).
(25) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).
(26) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).
(27) C. K. Jørgensen, *Advan. Chem. Ser.*, **No. 62**, 161 (1967).
(28) C. K. Jørgensen, *Chem. Phys. Lett.*, **3**, 380 (1969).

taneous picture (10^{-13} sec) of much lower symmetry. Other techniques of measurement, such as paramagnetic resonance at a given temperature, may show an intermediate time scale. Thus, $Cu(H_2O)_6{}^{2+}$ in certain salts shows time-average cubic symmetry at room temperature but tetragonal symmetry (four short and two long Cu–O distances) at the temperature of liquid air. The visible spectrum indicates a strong tetragonal distortion, presumably due to a first-order Jahn–Teller effect.[7,14]

There is no doubt that s–p mixing is important in the lone pairs of certain diatomic molecules such as BH, CO, and N_2. The Gillespie effect is weak or absent in d-group complexes. The intensities of parity-forbidden inter-subshell transitions come from vibronic coupling with odd excited states,[29] which are normally electron-transfer bands due to reducing ligands, as discussed below. Even at $0°K$, the instantaneous symmetry is generally C_1, though it is *almost* holohedric. However, the stereochemistry of many $3d^9$ copper(II)[30] and $4d^8$ palladium(II)[31-33] complexes is rather unusual, such as square-pyramidal $Cu(NH_3)_4H_2O^{2+}$ and $Cu(NH_3)_5{}^{2+}$ and approximately quadratic *cis*-$Pd^{II}N_2X_2$ and may be connected with l mixing, as well as the unexpected high intensity of the inter-subshell transitions.

Only a few instances are known of mixing of even l values. The lone pair ($3z^2 - r^2$) of the quadratic $5d^8$ complex $PtCl_4{}^{2-}$ seems to be depleted[34] in the molecular plane by mixing with the empty 6s orbital. On the other hand, linear d^{10} complexes[35] formed by copper(I), silver(I), gold(I), and mercury(II) seem to be stabilized by this mixing with opposite sign of the coefficient to the empty s orbital, concentrating electronic density in the equatorial plane.

Persistence of One-Electron Orbitals in X-Ray and Photoelectron Spectra

Nowhere is the persistence of atomic orbitals in compounds as clear as in the case of inner shells studied by X-ray spectra. As discussed in Chapter 12 of ref 3, all the inner shells of the same atom show almost the same *chemical shift*, dI, of the ionization energy I. Hence the sharp emission lines due to jumps of an electron from one shell to a vacant position in another shell show only small chemical shifts. Since most compounds decompose if they are used as anticathode in an X-ray tube, the most reliable technique for studying emission spectra is X-ray fluorescence. The absorption bands due to transitions to empty or partly filled orbitals are much broader, but show chemical shifts comparable to the variation of the ionization energy of the loosest bound

electrons going from one compound to another of the same element.[36] It is a considerable experimental difficulty that only few compounds can be prepared as thin, homogeneous films for this purpose. It is therefore most useful that *photoelectron spectroscopy* recently has been developed, giving essentially the same information as X-ray absorption spectra, for gaseous (volatile) and solid samples, in the superficial layer about 100 Å thick.

Actually, Turner[37,38] studied gaseous samples under low pressure, using monochromatic helium radiation at 584 Å (corresponding to 21.2 eV), and measured the kinetic energy of the ejected electrons with a differential device, indicating the difference between 21.2 eV and the ionization energy, I, of the orbital. Whereas many other techniques are available for studying the lowest ionization energy of a gaseous system, representing the threshold for photoconductivity as a function of the wave number of monochromatic radiation, this is the best opportunity available for studying the ionization energies, I, of *penultimate orbitals*. The I values of a given molecule (showing vibrational structure under high resolution) can be compared with MO calculations. Furthermore, the delocalized MO of halides such as CF_4, CCl_4, SF_6, WF_6, or other complexes such as $V(CO)_6$, $Cr(CO)_6$, $HMn(CO)_5$, and $Fe(C_5H_5)_2$ can be compared with *electron-transfer spectra* in the visible and the ultraviolet.[39,40] In the case of reducing halide ligands and oxidizing central atoms, the wave number indicating

$$I(a) - I(b) + J(b,b) - J(a,b) \qquad (11)$$

can be used[3,39] for evaluating the *optical electronegativity*, x_{opt}, of X^- and of M in a definite oxidation state.[4] The optical transition a → b does not give exactly the difference between the two ionization energies $I(a)$ and $I(b)$ accessible for photoelectron spectroscopy but that corrected by the two integrals of interelectronic repulsion, $J(b,b) - J(a,b)$. If orbital b is empty, $I(b)$ is defined from the fact that the electron affinity of b is $I(b) - J(b,b)$. Photoelectron studies of organic molecules have been reported,[41] and a review has been published in this journal.[42]

However, a far more extensive range of I values can be studied using soft X-rays such as the 2p → 1s transition of magnesium (9.87 Å or 1253 eV) or aluminum (8.32 Å or 1486 eV).[43,44] Originally, it was thought[45] that the chemical shift, dI, of inner shells of a given ele-

(29) R. F. Fenske, *J. Amer. Chem. Soc.*, **89**, 252 (1967).

(30) V. Romano and J. Bjerrum, *Acta Chem. Scand.*, **24**, 1551 (1970).

(31) L. Rasmussen and C. K. Jørgensen, *ibid.*, **22**, 2313 (1968).

(32) L. Rasmussen and C. K. Jørgensen, *Inorg. Chim. Acta*, **3**, 547 (1969).

(33) H. H. Schmidtke and C. K. Jørgensen, *Chem. Phys. Lett.*, **5**, 202 (1970).

(34) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

(35) C. K. Jørgensen and J. Pouradier, *J. Chim. Phys. Physicochim. Biol.*, **67**, 124 (1970).

(36) C. Bonnelle in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Wiley, London, 1968, p 45.

(37) D. W. Turner in ref 36, p 74.

(38) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970.

(39) C. K. Jørgensen, *Halogen Chem.*, **1**, 265 (1967).

(40) C. K. Jørgensen, *Progr. Inorg. Chem.*, **12**, 101 (1970).

(41) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

(42) A. D. Baker, *Accounts Chem. Res.*, **3**, 17 (1970).

(43) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindgren, "ESCA-Atomic, Molecular and Solid State Structure Studies by Means of Electron Spectroscopy," Almqvist and Wiksell, Uppsala, 1967.

ment was essentially a linear function of the oxidation state, 9.6 eV from europium(II) to europium(III) and, more moderate, 6.3 eV from iodide($-$I) to iodine(VII). However, a large number of nitrogen compounds[46] show a variation of I of the 1s orbital from 399 eV for NH_3 to 407 eV for NO_3^-. Kramer and Klein[47] clearly demonstrated that the variation of I for 3p from 52.4 eV in iron metal to 57.7 eV in K_3FeF_6 and in K_2FeO_4 depends not only on the oxidation state of Fe but also on the extent of covalent bonding, iron(III) dithiocarbamate $[Fe(S_2CN(C_2H_5)_2)_3]$ having $I = 53.4$ eV. It might be argued that dI is a measure of the fractional[4,12] atomic charge, δ, but a closer analysis shows that dI is essentially the change of the Hartree potential $U(x,y,z)$ at the position of the nucleus of the atom considered. In a system $M^{\delta+}(X^{\delta-/N})_N$ with m electrons in the outer shell with average reciprocal radius $\langle r^{-1}\rangle_0$ in the neutral atom M^0, the $(m - \delta)$ electrons in the compound with the M–X distance R produce

$$dI = \delta\langle r^{-1}\rangle_0 - m\delta\frac{\partial\langle r^{-1}\rangle}{\partial\delta} - \frac{\delta}{R} \qquad (12)$$

proportional to δ but where the positive contribution from external screening is counteracted by the differential change of $\langle r^{-1}\rangle$ with δ and by the Madelung term $-\delta/R$. The much smaller dI observed in compounds than that calculated for gaseous M^{z+} (not having a Madelung potential) should not be taken as an argument for small δ. There is no doubt that photoelectron spectroscopy is going to be a technique of utmost importance, not only for surface chemistry and the study of solid catalysts but also for the understanding of chemical bonding.

Physicists in Uppsala[44] have also detected the two different $I = 543.1$ and 544.2 eV of 1s of the oxygen molecule, corresponding to the formation of $S = {}^3/_2$ and $^1/_2$, respectively, from the ground state of O_2 having $S = 1$. This effect should be present in d- and f-group compounds having positive S and has recently been reported for manganese(II), iron(III), and manganese(IV) oxides and fluorides,[48] ionizing 3s and 3p.

From the point of view of quantum mechanics, it is surprising enough that the X-ray absorption bands or the photoelectron peaks are so narrow (well below 1 eV) because they are technically *autoionizing*, situated in the continuum of E values above the first ionization energy of the system. Russell discovered narrow energy levels of the calcium atom belonging to the configuration [Ar]3d4d at higher energy than the ground state [Ar]4s of Ca$^+$. The empirical manifestation of penulti-

mate orbitals and inner shells in photoelectron spectroscopy is highly interesting, lending support to a one-electron description of the ionization process both in monatomic and polyatomic entities. In a not too broad I interval, the photoelectron peaks have areas roughly proportional to the number of electrons, though weak tendencies toward selection rules for the ionization exist,[43,44] but 1486-eV excitation has particularly strong 4f ionization probability for $Z > 72$, and the probability for ionization of different inner shells can be highly different.

Conclusions

The one-electron AO and MO descriptions of the states of atoms and molecules are protected by a set of unexpected circumstances like a Chinese egg. First of all, perturbation theory ensures that the *number* of discrete eigenvalues E with definite symmetry type is not changed as a result of the moderate stabilization due to configuration interaction, and that the $(2l + 1)$ orbitals of a given shell with given symmetry type γ_n (or λ in linear symmetries) still can be recognized after formation of MO by moderate delocalization on neighbor atoms. Secondly, the Hartree potential can be expanded in a rapidly convergent series (eq 10) according to generated subgroup symmetries giving a physical interpretation of the subtraction of the specific properties of a given subgroup from those of its supergroup (our subject, the persistence of atomic orbitals, is the approximate conservation of l values in spherical relevant symmetry). Third, during the thermal vibration of a molecule, the molecule *almost* conserves the high symmetry of its equilibrium internuclear distances (producing the selection rules for infrared and Raman spectra). This is true in the sense that the residual Hartree potential $U[-G] = U - U[+G]$, after the generation of the high symmetry, G, is numerically small. Electronic transitions, however, are so rapid that an instantaneous picture is obtained. Fourth, the external world and next-nearest neighbor atoms almost exclusively show their influence *via* the Madelung potential, $V(x,y,z)$.

We have deliberately talked about l mixing in MO's of definite γ_n in the relevant symmetry and not *hybridization*. The main difficulty[14] for conventional hybridization theory is that, whereas the radial functions R_{2s} and R_{2p} of eq 7 in boron, carbon, and nitrogen are not extremely different, it is not possible to put a common radial function outside parentheses in d^2sp^3 or dsp^2 hybridizations.

It is frequently argued that the one-electron functions ψ in a closed-shell Ψ to a large extent are arbitrary in the sense that Ψ is invariant to a unitary transformation of the set of ψ. This is a very dangerous argument, since the actual Ψ *is not* a well-defined configuration though it belongs to a preponderant configuration, and by ionization (*e.g.*, photoelectron) and excitation (*e.g.*, visible spectroscopy) processes, the appropriate ψ can be recognized. These orbitals would be the eigenvectors of an effective one-electron operator if a quantitative MO theory could be constructed. At least, they are

(44) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.
(45) C. S. Fadley, S. B. M. Hagström, J. M. Hollander, M. P. Klein, and D. A. Shirley, *Science*, **157**, 1571 (1967).
(46) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969); J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, **3**, 193 (1970).
(47) L. N. Kramer and M. P. Klein, *J. Chem. Phys.*, **51**, 3618 (1969).
(48) C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Lett.*, **23**, 1397 (1969).