The Orbital Concept in Molecular Spectroscopy[†]

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A. Introduction

Chemistry is suffused by molecular orbital (MO) concepts. On a theoretical level, these concepts may be either highly sophisticated or blatantly heuristic.

The MO concept, being an approximation, runs into certain difficulties. These difficulties occur in greatest profusion at the interface of theory and experiment. It turns out that experiment, in the form of electronic and electron spectroscopy,[1-3] provides direct information for the many-electron, ground and excited states, and *not* for the one-electron molecular orbitals. In any event, the relationship of the experimental state information to the conceptual orbital considerations has proceeded apace, often in very qualitative and empirical ways. And, as a result, one finds oneself in the odd situation of possessing considerable insight, yet suffering from a great deal of confusion.

This essay is an attempt to resolve some of that confusion. It is excerpted from a series of lectures on photoelectron spectroscopy which we presented at LSU in the fall of 1975. In the course of these lectures, we ran into some troubles.[4] In brief, we were unable to refer our students to any comprehensive, yet comprehensible sources which dealt with the following:

(i) Chemistry, particularly organic chemistry is more and more dependent on MO concepts. One of the more pervasive of these, namely orbital interactions, is usually exemplified quite heavily but is rarely discussed in terms of any meaningful MO theory.

(ii) The various electronic orbital types are labeled, in self-evident terminology and in the approximate order of decreasing binding energy: "core", "valence", and "Rydberg". The interrelations of these types of orbitals are rarely, if ever, specified. Nor is the manner of their evolution from the same energy operator ever delineated.

(iii) Many significant theorems, Koopmans', for example, are derived in passing (so to speak), not derived at all, or even derived wrongly. Such observations, coupled with student questions and frustrations, provided the goad for this essay.

Our aim is to relate orbital properties to state properties in a way which is useful and meaningful. Consequently, we begin with the general many-electron, many-nuclei problem. While retaining as much rigor as is warranted, we proceed to a discussion of certain trenchant theorems, their derivations, and the approximations inherent in their use. In this connection, we pay considerable attention to Koopmans' theorem, to its extension to core ionization events, and to its utility in discussing nonionizing electronic excitations of core, valence, and Rydberg types. Finally, we attempt to unify the subject of orbital interactions and, in the process, to discern the theoretical content of the intuitive concepts in which this area abounds.

In any attempt as broad as this, some compromise is usually required. Thus, we will evade all discussions of computational techniques and experimental apparatus, and for the same reasons: computational and experimental techniques are of interest only to the extent that they bear on the orbital concept.

For the sake of cohesion, we will limit ourselves to molecules with closed-shell ground states, and we will restrict ourselves to electronic excitation events which are induced by photons.[5]

1. Orbital Classification Scheme

Orbitals, or electrons, are readily categorized as "core", "valence", or "Rydberg". This categorization depends on differences of the binding energies and the spatial extents of the orbitals, and is approximate. It is illustrated in Table I.

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TABLE I. Various Orbital Regimes

Orbital regime	Binding energy (absolute), cm^{-1}	Major energy contribution (zero-order)	Minor energy contribution (perturbation)	Orbital extent
Core	$\geq 10^6$ [a]	Attraction by one particular nucleus	Neighboring nuclei; valence electrons	Atomic-like; tightly packed around one particular nucleus; localized
Valence				
Bonding	1-5 $\times 10^5$	"Whole molecule" in nature		Delocalized; of same size as molecule
Lone pair	5-10 $\times 10^4$	Attraction by one particular nucleus and its complement of core electrons	Remainder of the molecule	Localized
Antibonding (virtual)	$\leq 4 \times 10^4$	"Whole molecule" in nature		Delocalized; of same size as molecule
Rydberg	$\leq 3 \times 10^4$	Attraction by whole molecule acting as a point charge	Penetration of core; deviation of potential from spherical symmetry	Atomic-like large; diffuse; hypermolecular

[a] Except lithium, for which $IE_{1s} = 0.44 \times 10^6$ cm^{-1}.

TABLE II. A Glossary of Notations

	Wave Functions
$\Psi = \Psi(\mathbf{x},\mathbf{R})$	the general many-electron wave function
$\Psi_{el} = \Psi(\mathbf{x};\mathbf{R})$	the many-electron wave function in the "fixed-nucleus" approximation
$\psi = \psi(\mathbf{x};\mathbf{R})$	a many-electron Slater determinant wave function
$\varphi = \varphi(\mathbf{x}_1;\mathbf{R})$	a molecular spin orbital
$\phi = \phi(\mathbf{r}_1;\mathbf{R})$	a molecular (space) orbital
$\alpha(\omega_1)$, $\beta(\omega_1)$	spin functions for $m_s = 1/2$ and $-1/2$, respectively.
$\chi = \chi(\mathbf{x}_{1A})$	an atomic spin orbital
$\Xi = \Xi(\mathbf{R})$	a nuclear wave function
$\psi_0 = \lvert\varphi_a\varphi_b\varphi_c \ldots \varphi_l\varphi_m\varphi_n\rvert$	determinant for the ground configuration
$\psi_{-m} = \lvert\varphi_a\varphi_b\varphi_c \ldots \varphi_l\varphi_n\rvert$	determinant for a Koopmans' configuration
$\psi_m^\nu = \lvert\varphi_a\varphi_b\varphi_c \ldots \varphi_l\varphi_\nu\varphi_n\rvert$	determinant for a singly excited configuration
$\varphi_{lm}^{\mu\nu} = \lvert\varphi_a\varphi_b\varphi_c \ldots \varphi_\mu\varphi_\nu\varphi_n\rvert$	determinant for a doubly excited configuration
$\tilde{\varphi}$	an optimum virtual molecular spin orbital
	Coordinates
$\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \ldots\} = \{1, 2, \ldots\}$	the space and spin coordinate set for electrons 1, 2, . . .
$\mathbf{x}_1 = \{\mathbf{r}_1,\omega_1\}$	the space and spin coordinate set for electron 1
$\mathbf{r}_1$	electronic space coordinate set for electron 1
ω_1	electronic spin coordinate for electron 1
$\mathbf{R} = \{\mathbf{R}_A, \mathbf{R}_B, \ldots\}$	nuclear space coordinate set

	Subscripts and Superscripts
$a, b, c, \ldots, k, l, m, n$	occupied (spin) orbitals of ground configuration
$\mu, \nu, \ldots$	unoccupied (or virtual) (spin) orbitals
A, B, C, . . .	nuclei or submolecular parts
$i, j, \ldots$	electron numbering
	Operators
$\mathcal{H}$	general Hamiltonian
$\mathcal{H}_{el}$	electronic Hamiltonian
$\mathcal{H}^c$	core Hamiltonian; the one-electron part of $\mathcal{H}_{el}$
$\mathcal{F}$	Fock operator
$\mathcal{F}_m$	Fock operator with spin orbital φ_m of ψ_0 deleted
$\mathcal{T}$	kinetic energy operator
$\mathcal{P}_{12}$	permutation operator which interchanges coordinates of electrons 1 and 2
$\Omega(i)$	general one-electron operator
$\Omega(i,j)$	general two-electron operator

Miscellaneous

$\delta_{ij} = 1$ (or zero) for $i = j$ (or $i \neq j$) Kronecker delta

$\langle\varphi_i|\varphi_j\rangle = \int \varphi_i^*(1)\varphi_j(1)\, d\mathbf{x}_1$

$$\langle\varphi_a\varphi_b|(1 - \mathcal{P}_{12})/r_{12}|\varphi_c\varphi_d\rangle = \int\int \varphi_a^*(1)\varphi_b^*(2)[\varphi_c(1)\varphi_d(2) - \varphi_c(2)\varphi_d(1)] \frac{1}{r_{12}}\, d\mathbf{x}_1 d\mathbf{x}_2$$

N	total number of electrons
Z_A	atomic number of atom A
S	total spin quantum number
M_S	component of S along a particular axis

The core-electron binding energies characterize the atom. Thus, when the atom is part of a molecule, the perturbation of the core binding energy by all the other atoms in the molecule environment rarely exceeds 10%; in fact, it is usually considerably less. In absolute terms, the perturbation lies in the range $0.001-0.1 \times 10^6$ cm^{-1}. One could say that the core orbitals are so compressed about their specific atomic centers that all neighboring atomic centers of the molecule, being quite far away, exert only a small perturbative influence.

On the other extreme are the Rydberg orbitals. The binding energy of a Rydberg electron is quite small, usually $<3 \times 10^4$ cm^{-1}. Indeed, the highly excited Rydberg electron behaves as a quasi-hydrogenic electron whose binding energy is given by $Z^2R/(n^*)^2$, where R is the Rydberg constant, n^* is an effective principal quantum number, and Z is the charge "seen" by the Rydberg electron. One could say that Rydberg orbitals are so large spatially that the details of molecular architecture become insignificant and merely exert perturbative effects on an otherwise hydrogenic electron.

The valence electrons, for the most part, are intermediate in energy and spatial extent. They represent a coupling domain which is uniquely molecular. In specific, they are not so tightly bound that they can be considered to be "nearly atomic" (i.e., core) electrons, nor so weakly bound that they can be supposed to be "quasi-hydrogenic" (i.e., Rydberg) electrons. As a result, it is the valence electrons which pose the most difficult theoretical problem. In fact, if a good discussion of the valence electron problem were available, it should be possible, by appropriate extension or shrinkage of the valence orbitals, to extract a pertinent description of the Rydberg electron or core electron extremes, respectively. Consequently, we will begin our discussion with the valence MO's.

There is another reason, however, for starting with the valence orbitals. The valence orbitals are the "uniquely molecular" orbitals. For example, they determine chemical bonding characteristics, molecular structure, and the characteristics of chemical reactions. It is not surprising, then, that very many subcategorizations of them exist and that discussions of them are heavily laced with empirical and heuristic connotations. The removal of these connotations and/or their replacement with theoretically valid and empirically useful concepts is another one of the major aims of this essay.

A glossary of the notations used in this work is given in Table II.

B. The MO Approximation

One of the aims of quantum chemistry is to solve the time-independent Schrödinger equation

$$\mathcal{H}(\mathbf{x},\mathbf{R})\Psi(\mathbf{x},\mathbf{R}) = E\Psi(\mathbf{x},\mathbf{R}) \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian operator. Both $\mathcal{H}$ and Ψ, as indicated in Table II, depend on the coordinates of all nuclei and all electrons in the molecule. The goal of this section is to simplify the multidimensional problem of eq 1, to reduce it, if possible, to one which is dependent on the coordinates of only one electron.

We neglect, for convenience, all relativistic terms in $\mathcal{H}$ and rewrite it as

$$\mathcal{H}(\mathbf{r},\mathbf{R}) = \sum_{A} \mathcal{T}_A + \sum_{A<B} Z_A Z_B/R_{AB} + \sum_{i} \mathcal{T}_i + \sum_{i<j} 1/r_{ij} - \sum_{i}\sum_{A} Z_A/r_{iA} \tag{2}$$

The terms of eq 2, in order of appearance, describe the kinetic energy of the nuclei, the electrostatic repulsion of the nuclei, the kinetic energy of the electrons, the electron–electron repulsion, and the nuclear–electron attraction.[6]

1. Separation of Nuclear and Electronic Motions

The first step is to approximate $\Psi(\mathbf{x},\mathbf{R})$ by a product such that one of the parts is only weakly dependent on **R**:

$$\Psi(\mathbf{x},\mathbf{R}) = \Psi(\mathbf{x};\mathbf{R})\Xi(\mathbf{R}) \tag{3}$$

The function $\Psi(\mathbf{x};\mathbf{R})$, which is dependent on **R** only in a parametric fashion, is known as the electronic wave function. The function $\Xi(\mathbf{R})$ is known as the nuclear wave function. These functions are determined by

$$\mathcal{H}_{el}\Psi_{el}(\mathbf{x};\mathbf{R}) = E_{el}(\mathbf{R})\Psi_{el}(\mathbf{x};\mathbf{R}) \tag{4}$$

$$\mathcal{H}_{n}\Xi(\mathbf{R}) = E\Xi(\mathbf{R}) \tag{5}$$

where the Hamiltonian operators, to the exclusion of relativistic effects, are given by

$$\mathcal{H}_{el} = \sum_{i} \mathcal{T}_i + \sum_{i<j} 1/r_{ij} - \sum_{i}\sum_{A} Z_A/r_{iA} + \sum\sum_{A<B} Z_A Z_B/R_{AB} \tag{6}$$

$$\mathcal{H}_{n} = \sum_{A} \mathcal{T}_A + E_{el}(\mathbf{R}) \tag{7}$$

Relative to eq 3, eq 4–7 involve approximations[7] such as the neglect of various cross terms, e.g.,

$$\langle \Psi_{el}(\mathbf{x};\mathbf{R})|\mathcal{T}_A|\Psi_{el}(\mathbf{x};\mathbf{R})\rangle$$

This separation into an electronic and a nuclear part is known as the Born-Oppenheimer approximation.[8] It permits the use of several well-known concepts. These are:

Electronic state. The energy of an electronic state is dependent on **R** and this dependence yields the familiar potential energy well which governs vibrational motion.

Equilibrium nuclear geometry. This geometry is defined as that which exists at the absolute minimum of the (multidimensional) potential energy surface $E_{el}(\mathbf{R})$.

Electronic energy and vibrational energy. The energy separates into distinct electronic and vibrational parts.

All these concepts lose validity when eq 3 is not a good approximation to the solutions of eq 1. Thus, the Born-Oppenheimer approximation will usually be invalid when the energy differences between electronic states are smaller than the vibrational energy increments associable with any of the electronic states. In particular, when the electronic states are nonaccidentally degenerate, Jahn-Teller or Renner instabilities[8] will arise from a coupling of the electronic and vibrational motions.

In a more mechanistic vein, the possibility of a separation into distinct nuclear and electronic motions is based on the comparatively larger mass of the nuclei: the electrons have less inertia and can adjust their motions, more or less instantaneously, to any rearrangement of the nuclear positions.

2. Independent Particle Approximation

The electronic wave function $\Psi_{el}(\mathbf{x};\mathbf{R})$ is still dependent on the coordinates of all electrons. If a complete set of orthonormal, many-electron wave functions $\{\psi_i\}$ is available, $\Psi_{el}(\mathbf{x};\mathbf{R})$ can be expanded as

$$\Psi_{el}(\mathbf{x};\mathbf{R}) = \sum_{i} \psi_i c_i \tag{8}$$

where

$$\langle \psi_i|\psi_j\rangle = \delta_{ij} \tag{9}$$

We now investigate such an expansion, the manner of its simplification, and the nature of the functions ψ_i.

a. Determinantal Wave Functions

The Pauli principle dictates that $\Psi_{el}(\mathbf{x};\mathbf{R})$ must be antisymmetric with respect to any interchange of electron coordinates. Given the abbreviations

$$\Psi_{el}(\mathbf{x};\mathbf{R}) \equiv \Psi_{el}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_i,\ldots;\mathbf{R}) \equiv \Psi_{el}(1,2,\ldots,i,\ldots;\mathbf{R})$$

the antisymmetry requirement is

$$\Psi_{el}(1,2,3,\ldots,i,\ldots,k,\ldots;\mathbf{R}) = -\Psi_{el}(1,2,3,\ldots,k,\ldots,i,\ldots;\mathbf{R}) \tag{10}$$

Since antisymmetry is one of the more unique characteristics of determinantal wave functions, one convenient and complete set of many electron functions is provided by a set of Slater determinants built from a complete set of spin orbitals $\{\varphi_i(j;\mathbf{R})\}$.

$$\psi(1,2,\ldots,N;\mathbf{R}) = \frac{1}{(N!)^{1/2}}\begin{vmatrix} \varphi_a(1;\mathbf{R}) & \varphi_b(1;\mathbf{R}) & \varphi_c(1;\mathbf{R})\ldots\varphi_n(1;\mathbf{R}) \\ \varphi_a(2;\mathbf{R}) & \varphi_b(2;\mathbf{R}) & \varphi_c(2;\mathbf{R})\ldots\varphi_n(2;\mathbf{R}) \\ \varphi_a(3;\mathbf{R}) & \varphi_b(3;\mathbf{R}) & \varphi_c(3;\mathbf{R})\ldots\varphi_n(3;\mathbf{R}) \\ \vdots & & \vdots \\ \varphi_a(N;\mathbf{R}) & \varphi_b(N;\mathbf{R}) & \varphi_c(N;\mathbf{R})\ldots\varphi_n(N;\mathbf{R}) \end{vmatrix} \tag{11}$$

$$= |\varphi_a(1;\mathbf{R})\varphi_b(2;\mathbf{R})\varphi_c(3;\mathbf{R})\ldots\varphi_n(N;\mathbf{R})| = |\varphi_a\varphi_b\varphi_c\ldots\varphi_n| \tag{12}$$

Since the electron-occupancy number of any spin orbital is either *one* or *zero*, it follows that the number of occupied spin orbitals equals the number of electrons. The functions φ_i depend on the coordinates of one electron only; they are termed "spin orbitals".[9] If the set of spin orbitals $\{\varphi_i\}$ is complete and, for convenience, orthonormal,[10] it may be shown that the set of all possible determinants, $\{\psi_i\}$, which is constructed from these spin orbitals is also complete and orthonormal.

TABLE III. A Collection of Pertinent Slater Rules[a]

Overlap

$$\langle \psi_0 | \psi_0 \rangle = 1$$

$$\langle \psi_0 | \psi_k^\mu \rangle = \langle \psi_0 | \psi_{kl}^{\mu\nu} \rangle = 0$$

One-Electron Operators

$$\left\langle \psi_0 \middle| \sum_i \Omega(i) \middle| \psi_0 \right\rangle = \sum_{k \in \text{occ}} \langle \varphi_k(1) | \Omega(1) | \varphi_k(1) \rangle$$

$$\left\langle \psi_0 \middle| \sum_i \Omega(i) \middle| \psi_k^\mu \right\rangle = \langle \varphi_k(1) | \Omega(1) | \varphi_\mu(1) \rangle$$

$$\left\langle \psi_0 \middle| \sum_i \Omega(i) \middle| \psi_{kl}^{\mu\nu} \right\rangle = 0$$

Two-Electron Operators

$$\left\langle \psi_0 \middle| \sum_{i<j} \Omega(i,j) \middle| \psi_0 \right\rangle = \sum_{k<l \in \text{occ}} \{ \langle \varphi_k(1)\varphi_l(2) | \Omega(1,2) | \varphi_k(1)\varphi_l(2) \rangle - \langle \varphi_k(1)\varphi_l(2) | \Omega(1,2) | \varphi_k(2)\varphi_l(1) \rangle \}$$

$$\left\langle \psi_0 \middle| \sum_{i<j} \Omega(i,j) \middle| \psi_l^\mu \right\rangle = \sum_{k \in \text{occ}} \{ \langle \varphi_k(1)\varphi_l(2) | \Omega(1,2) | \varphi_k(1)\varphi_\mu(2) \rangle - \langle \varphi_k(1)\varphi_l(2) | \Omega(1,2) | \varphi_k(2)\varphi_\mu(1) \rangle \}$$

$$\left\langle \psi_0 \middle| \sum_{i<j} \Omega(i,j) \middle| \psi_{kl}^{\mu\nu} \right\rangle = \langle \varphi_k(1)\varphi_l(2) | \Omega(1,2) | \varphi_\mu(1)\varphi_\nu(2) \rangle - \langle \varphi_k(1)\varphi_l(2) | \Omega(1,2) | \varphi_\mu(2)\varphi_\nu(1) \rangle$$

$$\left\langle \psi_0 \middle| \sum_{i<j} \Omega(i,j) \middle| \psi_{klm}^{\mu\nu\rho} \right\rangle = 0$$

[a] For definition of $\Omega(i)$ and $\Omega(i,j)$, see Table II.

We now subdivide the set of determinantal wave functions in a very specific way. The ground-state configuration,[11] ψ_0, is obtained by placing the N electrons, one at a time, into the n most tightly bound spin orbitals. Singly excited configuration functions, ψ_k^μ, are obtained by promoting an electron from the kth to the μth most tightly bound spin orbital. Doubly excited configuration functions are generated by the promotion of two electrons out of the spin orbitals contained in ψ_0, etc. These classes of determinantal functions are defined as

$$\begin{aligned} \psi_0 &= |\varphi_a\varphi_b \ldots \varphi_k \ldots \varphi_l \ldots \varphi_n| \\ \psi_k^\mu &= |\varphi_a\varphi_b \ldots \varphi_\mu \ldots \varphi_l \ldots \varphi_n| \\ \psi_{kl}^{\mu\nu} &= |\varphi_a\varphi_b \ldots \varphi_\mu \ldots \varphi_\nu \ldots \varphi_n| \end{aligned} \tag{13}$$

The expansion of eq 8 is now rewritten as

$$\Psi_{\text{el}} = \psi_0 c_0 + \sum_{k,\mu} \psi_k^\mu c_k^\mu + \sum_{\substack{k,l \\ \mu,\nu}} \psi_{kl}^{\mu\nu} c_{kl}^{\mu\nu} + \ldots \tag{14}$$

The expansion of eq 14 is known as the CI (configuration interaction) expansion. This expansion does not contain any approximation beyond those of eq 3–5.

b. The Hartree–Fock Operator

It would be very convenient if we could choose the set of spin orbitals, $\{\varphi_i\}$, in such a way that, for the ground state, the coefficient c_0 would be approximately unity and others approximately zero. We now inquire into this possibility. In other words, we seek that set of spin orbitals, $\{\varphi_a, \varphi_b, \ldots, \varphi_n\}$, which gives the best approximation to the correct electronic wave function of the ground state while simultaneously retaining only the first term of eq 14. Equivalently, we wish to approximate the many-electron wave function $\Psi_{\text{el}}(\mathbf{x};\mathbf{R})$ of the ground state by a single Slater determinant.

The choice of the "best" Slater determinant involves the use of the "variation" principle: If the "best" Slater determinant were available, the electronic energy associated with it would be a minimum.[12] The expectation value of energy for a Slater determinant is given by Slater's rules.[13] These rules are presented in Table III. These lead to

$$\begin{aligned} E_{\text{el}} = \langle \psi | \mathcal{H}_{\text{el}} | \psi \rangle &= \sum_{k \in \text{occ}} \langle \varphi_k(1) | \mathcal{H}^{\text{c}}(1) | \varphi_k(1) \rangle \\ &\quad + \sum_{A<B} Z_A Z_B / R_{AB} \\ &\quad + \sum_{k<l \in \text{occ}} \langle \varphi_k(1)\varphi_l(2) | (1 - \mathcal{P}_{12})/r_{12} | \varphi_k(1)\varphi_l(2) \rangle \end{aligned} \tag{15}$$

where the summation indices, k or l, are members of the set of spin orbitals which are occupied in the configurational function of interest. The permutation operator $\mathcal{P}_{12}$ is defined as

$$\mathcal{P}_{12} | \varphi_k(1)\varphi_l(2) \rangle = | \varphi_k(2)\varphi_l(1) \rangle \tag{16}$$

and the core Hamiltonian, $\mathcal{H}^{\text{c}}(1)$, is defined by

$$\mathcal{H}^{\text{c}}(1) = \mathcal{T}_1 - \sum_A Z_A / r_{iA} \tag{17}$$

A variation of ψ_0 is produced by replacing some specific φ_i, where φ_i is a member of the set of occupied spin orbitals of ψ_0, by $\varphi_i + \delta\varphi_i$. The variation $\delta\varphi_i$ must be of such a nature that it does not disrupt any of the existing spin orbital orthonormalities; thus, we require

$$\langle \delta\varphi_i | \varphi_l \rangle = 0 \tag{18}$$

for all φ_l which are occupied. The consequent variation of total energy is given, following the Slater rules of Table III, as

$$\begin{aligned} \delta E_{\text{el},i} &= \langle \delta\varphi_i(1) | \mathcal{H}^{\text{c}}(1) | \varphi_i(1) \rangle \\ &\quad + \sum_{l \in \text{occ}} \langle \delta\varphi_i(1)\varphi_l(2) | (1 - \mathcal{P}_{12})/r_{12} | \varphi_i(1)\varphi_l(2) \rangle \end{aligned} \tag{19}$$

The restrictive conditions of eq 18 (which constrain the extremal problem of eq 19) lead, in Lagrangian undetermined multiplier form, to the conclusion that $E_{\text{el},i}$ is a minimum when

$$\delta E_{\text{el},i} - \sum_{l \in \text{occ}} \epsilon_{il} \langle \delta\varphi_i | \varphi_l \rangle = 0 \tag{20}$$

or, equivalently, when

$$\begin{aligned} &\langle \delta\varphi_i(1) | \mathcal{H}^{\text{c}}(1) | \varphi_i(1) \rangle \\ &\quad + \sum_{l \in \text{occ}} \langle \delta\varphi_i(1)\varphi_l(2) | (1 - \mathcal{P}_{12})/r_{12} | \varphi_i(1)\varphi_l(2) \rangle \\ &\quad = \sum_{l \in \text{occ}} \epsilon_{il} \langle \delta\varphi_i(1) | \varphi_l(1) \rangle \end{aligned} \tag{21}$$

Since the variations $\delta\varphi_i$ are arbitrary, by virtue of the implicit incorporation of the orthonormality restrictions of eq 18 into eq 20, we conclude that we have reached a stationary point if

$$\mathcal{F}(1)\varphi_i(1) = \sum_{l \in \text{occ}} \epsilon_{il} \varphi_l(1) \tag{22}$$

where $\mathcal{F}$, which is known as the Fock operator, is defined as

$$\mathcal{F}(1) \equiv \mathcal{H}^{\text{c}}(1) + \sum_{l \in \text{occ}} \int \mathrm{d}\mathbf{x}_2 \cdot \varphi_l^*(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_l(2) \tag{23}$$

The set of equations like eq 22, one for each φ_i in that set of spin orbitals which is occupied in ψ_0, is known as the Hartree–Fock set of equations.

c. The Self-Consistent Field

We have reached a time for pause. The multidimensional problem of eq 1 and 4 has been reduced to the formal one-electron problem of eq 22. However, whereas the derivation of the Hartree–Fock equations has been straightforward, solving this set of coupled equations is a more formidable task. Although formally one-electron, eq 22 depends on all other electrons because of the integals which occur in the Fock operator of eq

23. The method for solving these equations is known as the *self-consistent field* (SCF) method. One starts by guessing a set of spin orbitals $\{\varphi_i^{(0)}\}$, inserts these into eq 23 to obtain the Fock operator $\mathcal{F}^{(0)}$, and solves eq 22 for a new set of spin orbitals $\{\varphi_i^{(1)}\}$; this "first-improved" set of spin orbitals, $\{\varphi_i^{(1)}\}$, is reinserted into eq 23 to obtain a "first-improved" $\mathcal{F}^{(1)}$ and, thence, a "second-improved" set $\{\varphi_i^{(2)}\}$, etc. The cyclic iteration is repeated until self-consistency is reached, that is, until the difference $\{\varphi_i^{(m+1)}\} - \{\varphi_i^{(m)}\}$, or $|E_{\mathrm{el}}^{(m+1)} - E_{\mathrm{el}}^{(m)}|$, lies below some initially prescribed limit.

d. Canonical Spin Orbitals

Although the energy obtained by the Hartree–Fock SCF procedure is unique, the spin orbitals φ_i are not. This lack of uniqueness follows from the determinantal form of eq 11: the determinant of a matrix is invariant to a unitary transformation[14] of the matrix.

Thus, we are free to *choose* a very special set of spin orbitals, namely, that which reduces eq 22 to the simple form

$$\mathcal{F}(1)\varphi_i'(1) = \epsilon_{ii}\varphi_i'(1) = \epsilon_i\varphi_i'(1) \qquad (24)$$

This set of spin orbitals, which diagonalizes the matrix $\epsilon = (\epsilon_{ij})$, is known as the set of "canonical spin orbitals". The ϵ_i are known as the "spin orbital energies". The canonical set, as will be shown, acquires special significance with regard to electron excitation events.

The physical interpretation of the Hartree–Fock equations, in the form of eq 24, is especially simple. Equation 24 is a Schrödinger equation for an electron moving simultaneously in the field of the nuclei and in the average field produced by all other electrons. This *average* arises because of the integration performed in eq 23. A "self-interaction" is excluded because of the $1 - \mathcal{P}_{12}$ term, and the exchange term, $-\mathcal{P}_{12}$, takes care of antisymmetrization requirements.

It is appropriate to belabor a few points. These are:

The electronic Hamiltonian operator is *not* a sum of Fock operators. Thus,

$$\mathcal{H}_{\mathrm{el}}(1,2,3,\ldots,N) \neq \mathcal{F}(1) + \mathcal{F}(2) + \mathcal{F}(3) + \ldots + \mathcal{F}(N) \qquad (25)$$

As a result, we find

$$E_{\mathrm{el}} \neq \sum_i \epsilon_i \qquad (26)$$

It must be emphasized that the Hartree–Fock equations are merely the result of a condition which we impose on the spin orbitals in order to obtain the best possible electronic ground-state wave function in a single Slater-determinant format.

The use of orbital concepts such as "canonical orbital" or "orbital energy" does not imply the neglect of electron–electron interactions. These repulsions are explicitly introduced by the integrals which occur in the Fock operator of eq 23.

The probability of finding the 1st electron in the vicinity of a given coordinate, $\mathbf{x}_1$, is *not* given by $\varphi_1^*(\mathbf{x}_1)\varphi_1(\mathbf{x}_1)\,\mathrm{d}\mathbf{x}_1$. The correct expression is

$$\mathrm{d}\mathbf{x}_1\int\int\int\ldots\int\psi^*(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) \times \psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\,\mathrm{d}\mathbf{x}_2\mathrm{d}\mathbf{x}_3\ldots,\mathrm{d}\mathbf{x}_N$$

which reduces to

$$\sum_{l\in \mathrm{occ}} \varphi_l^*(\mathbf{x}_1)\varphi_l(\mathbf{x}_1)\,\mathrm{d}\mathbf{x}_1 \qquad (27)$$

Since the electrons are indistinguishable, this result should have been expected.

e. LCAO Approximation

Some comment concerning the manner of solving eq 24 is pertinent. Rather than solve the Hartree–Fock differential equations, these are first transformed to a matrix problem by introducing the *linear combination of atomic orbitals* (LCAO) approximation

$$\varphi_i = \sum_\alpha \chi_\alpha c_{\alpha i} \qquad (28)$$

where χ_α is an atomic spin orbital. The task of finding the energies ϵ_i and the molecular spin orbitals φ_k is thereby reduced to the matrix problem

$$\boldsymbol{Fc} = \boldsymbol{Sce} \qquad (29)$$

where

$$\boldsymbol{F} = (F_{\alpha\beta}) = (\langle\chi_\alpha|\mathcal{F}|\chi_\beta\rangle) \qquad (30)$$

$$\boldsymbol{S} = (S_{\alpha\beta}) = (\langle\chi_\alpha|\chi_\beta\rangle) \qquad (31)$$

$$\boldsymbol{e} = (\epsilon_{ij}) = (\epsilon_i\delta_{ij});\ \boldsymbol{c} = (c_{\alpha i}) \qquad (32)$$

Solutions are obtained from the secular determinant

$$|\boldsymbol{F} - \epsilon_i\boldsymbol{S}| = 0 \qquad (33)$$

The ϵ_i are obtained by diagonalization. The eigenvector $\boldsymbol{c}_i$, which is the adjoint of the row vector $(c_{1i},c_{2i},c_{3i},\ldots)$, is obtained by inserting ϵ_i into eq 29 and solving for the c_{ki}.

This LCAO approach has several advantages: it is convenient to program since it makes use of the powerful techniques of matrix algebra; the first set of orbitals (i.e., eigenvectors) can sometimes be guessed with some accuracy; since the molecular spin orbitals are expressed in terms of atomic spin orbitals, the concept of an "atom as part of molecule" becomes viable. As a result, all kinds of qualitative and semiquantitative notions which relate to our knowledge of atomic systems become feasible.

f. Restricted and Unrestricted Hartree–Fock

The final comment refers to the specific form employed for the one-electron eigenfunctions. So far, in fact, these have been spin orbitals. Since these spin orbitals are either singly occupied or not occupied at all, their use results in a very simple form for the various equations. However, we now wish to stress the implicit meaning of a *restricted* formalism. The restricted Hartree–Fock formalism, in the context of interest to us, consists of two parts:

(a) For each molecular spin orbital $\varphi_k(\mathbf{x}_1;\mathbf{R}) = \phi_k(\mathbf{r}_1;\mathbf{R})\alpha(\omega_1)$, where ϕ is a molecular orbital and α (or β) is the spin function for $m_S = \frac{1}{2}$ (or $-\frac{1}{2}$), there is another molecular spin orbital $\varphi_{k'}(\mathbf{x}_1;\mathbf{R})$ for which $\varphi_{k'}(\mathbf{x}_1;\mathbf{R}) = \phi_k(\mathbf{r}_1;\mathbf{R})\beta(\omega_1)$.

(b) Since the number of electrons, N, is even and since we have constrained our interests to "closed shells", it is well to be specific about what we mean by the term "closed-shell ground state". We assert that φ_k and $\varphi_{k'}$ are either both occupied (i.e., contained in the determinant which is optimized) or both unoccupied. Alternatively, all space orbitals ϕ_k in the determinant which is optimized are assumed to be either doubly occupied or not occupied at all. States with either double or zero occupancy of all space orbitals are known as "closed-shell" systems; otherwise, they are known as "open-shell".

Open-shell Hartree–Fock theory[15] is encumbered with several difficulties. We can attack the problem, or attempt to attack it, within the restricted Hartree–Fock formalism. Thus, we write

$$\varphi_k(\mathbf{x}_1;\mathbf{R}) = \phi_k(\mathbf{r}_1;\mathbf{R})\alpha(\omega_1)$$

$$\varphi_{k'}(\mathbf{x};\mathbf{R}) = \phi_k(\mathbf{r}_1;\mathbf{R})\beta(\omega_1) \qquad (34)$$

and, in this manner, permit occupation numbers of one, two, or zero for the space orbitals. The advantage of the restricted formalism of eq 34 is that it ensures that certain states can be represented correctly by a single Slater determinant. These

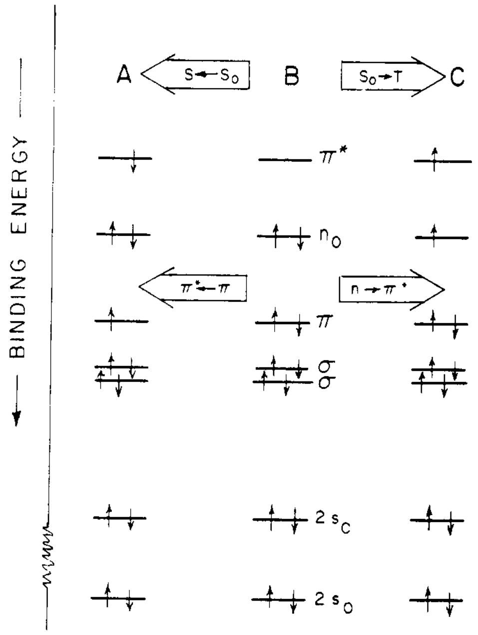


Figure 1. A configurational diagram showing the n → π* transition (which is denoted B → C) and the π → π* transition (which is denoted B → A) of formaldehyde (H_2CO). Except for the $2s_O$ and the π* MO's, the energies are obtained from experimental ionization energies [C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.*, **94**, 1451 (1972)]. A discussion of these transitions is available in ref 3d. The conventions employed in Figure 1 are standard. They are detailed in section I.C.1.

states are those for which the spin quantum numbers S and $|M_S|$ are maximal.

If we now drop the restriction of eq 34 and proceed to the unrestricted Hartree–Fock formalism, where $\varphi_{k'} = \phi_{k'}\beta$ with $\phi_{k'} \neq \phi_k$, this last advantage is lost. Specifically, since the unrestricted version allows different space orbitals for different spins, single determinantal wave functions are no longer eigenfunctions of the spin operator $\mathcal{S}^2$, when these represent nonclosed shell states. In the restricted version for S and $|M_S|$ not maximal, and in the unrestricted version for *all* S and $|M_S|$, a multideterminantal form must be used; otherwise, the wave function may not fulfill the basic permutation symmetry requirements. This leads immediately to noninteger occupation numbers for spin orbitals and, therefore, to a departure from the basic MO approximation.

Whether or not the restricted Hartree–Fock formalism, with its retention of integer occupation numbers, is embraced by the term "MO approximation" becomes a question of taste. It is for these reasons that we have confined ourselves to closed-shell systems.

g. Beyond the MO Approximation

It is now clear how one proceeds beyond the MO approximation. One merely includes more and more terms in the CI expansion of eq 14. The truncation of such an expansion, and the selection of the determinants which most efficiently truncate it, appears to be an art in itself. Finally, the actual computations are both expensive and labor-intensive, particularly when one seeks "really good" wave functions.

We provide one example. For this purpose, we use the medium-sized molecule H_2CS. First, however, we recall that the better calculation is the one which yields the lower total energy. A recent computation[16] for H_2CS gave a total energy of −11 878.068 eV, which is very close to the Hartree-Fock limit. Improvement of the wave function[17] by a very elaborate CI method decreased the total energy by 7.269 eV to yield −11 885.337 eV. This improvement, which amounts to 0.06%, could be considered to be minimal. However, in terms of chemical significance, 7.3 eV is indeed quite a large quantity of energy. In other words, while it is certainly comforting that the MO approximation accounts for 99.94% of the total energy, an error of 7.269 eV is not tolerable because chemistry deals with quantities of just this magnitude. Thus, whether one emphasizes the 0.06% or the 7.269 eV becomes a matter of taste.

C. Configuration Description of Electronic Excitation Processes

The approximations inherent in the MO concept, as detailed in section I.B, are straightforward. Before discussing their appropriateness, we will use the MO concept to describe different electronic states, and transitions among them. This description will reduce some of the more abstract concepts of section I.B to a familiar form.

As an example, consider the 3968-Å transition of formaldehyde, $H_2C^{18}O$. This transition is usually denoted n → π*. It is depicted in Figure 1 as B → C. It is clear that such diagrams can be drawn only when there is a very close resemblance between the orbitals which comprise the initial and final states. This singlet → triplet n → π* transition (and its singlet counterpart) is well known in a variety of carbonyl compounds where it can also be depicted as in Figure 1.

The singlet → singlet π → π* transition of H_2CO is also shown in Figure 1. It is denoted B → A. In contrast to the usefulness of the n → π* classification, the π → π* classification for carbonyls remains untested. Relevant data are scarce and secure assignments are unavailable.[19] It may well be that, in this instance, the single-configuration description for the $^1\pi\pi^*$ state is not very good.

Electronic spectroscopy deals with transitions between two different electronic states. As the example of Figure 1 indicates, if the MO concept is useful, it should permit the classification of both states by one (and only one) set of orbitals and by the set of occupation numbers {0,1,2}. Section I.C.1 will be concerned with such a classification scheme. As will be evident, the major impact of the MO approximation is that it provides a simple and useful way of classifying spectroscopic data. Thus, the idea of an orbital (or orbital energy) as a numerical convenience or as a first approximation to the results of a more elaborate treatment is merely a minor aspect of its overall utility.

1. Configuration Excitations

We describe excited states using a set of fixed orbitals and the set of occupation numbers, {0,1,2}. Our description is pictorial: The space orbital ϕ_k is a line on an energy diagram; the spin function α is represented by an "up-arrow", and β by a "down-arrow". The MO set consists of one core MO, three valence MO's which are fully occupied in the ground state, and two virtual MO's (either valence or Rydberg) which are unoccupied in the ground state. A set of selected configurations for systems containing N, $N + 1$, $N - 1$, and $N - 2$ electrons is shown in Figures 2A, 2B, 2C, and 2D, respectively. Some of the properties of these configurations are collected in Table IV.

Transitions between these configurations may be supposed to correspond to the energy differences measured by various spectroscopic techniques. The correspondence between the different types of configurational excitation and the various spectroscopic processes is illustrated further in Table V and Figure 3. Indeed, it was the correspondences of Table V which dictated the selection of configurations made in Figure 2. The processes of Table V are restricted to techniques which use photons as primary excitation means; however, all of them could be excited by other means.[5]

The terminology for the experimental processes (see Table V and Figure 3) is traditional and not necessarily logical. For

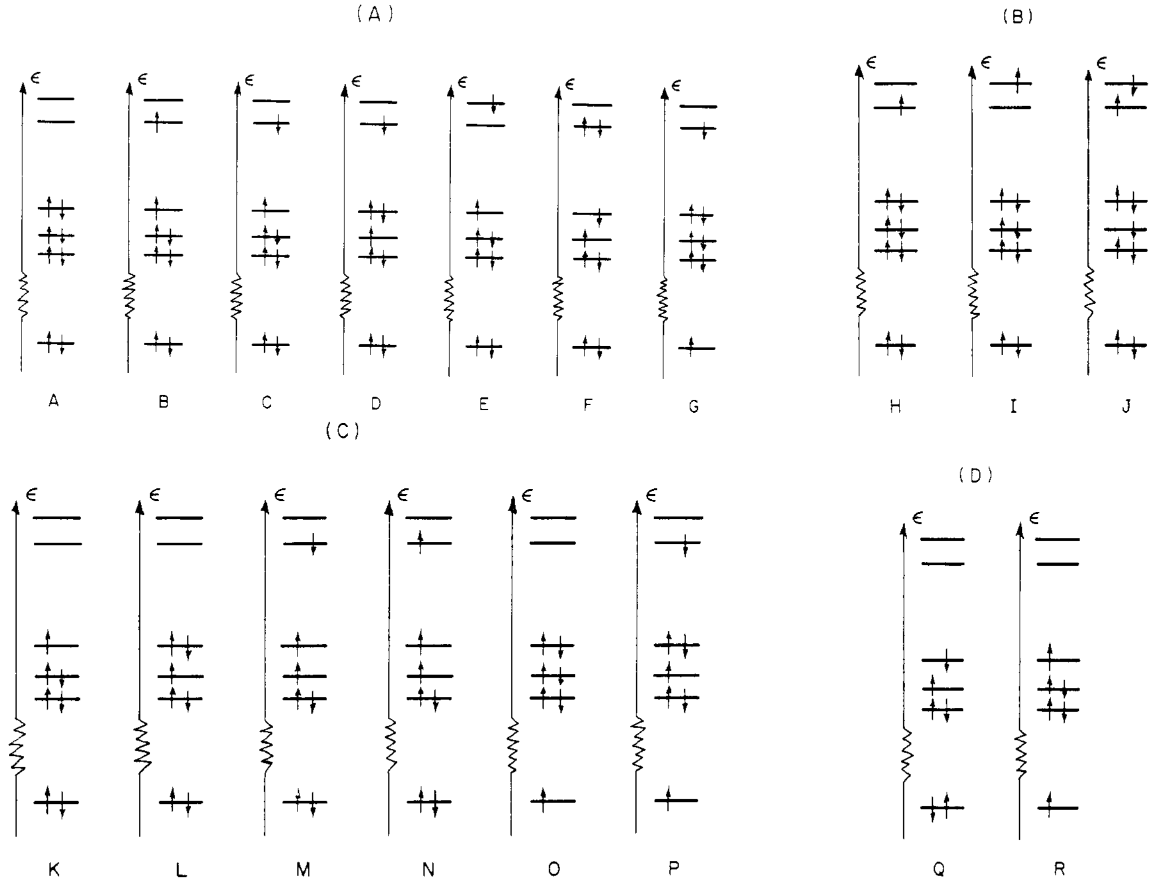


Figure 2. Electron configuration diagrams for a system containing one core MO, three valence MO's, and two virtual MO's: (A) $N = 8$ electrons, (B) $N = 9$ electrons, (C) $N = 7$ electrons, (D) $N = 6$ electrons. This figure suggests the possibility of a number of different sorts of experiment which have yet to be investigated. Furthermore, of the 18 × 17 = 306 possible transitions, only a very few will be discussed. The reader should consult Tables IV and V, Figure 3, and the text.

TABLE IV. The Electronic Configurations Depicted in Figure 2

Configuration	No. of electrons	M_S	S	Comments
A	N	0	0	Ground state
B	N	1	1	Lowest excited state; triplet
C	N	0	0, 1	Singly excited configurations; do not correspond to pure-spin states, but to mixtures of singlet and triplet states
D	N	0	0, 1	
E	N	0	0, 1	
F	N	0	0, 1	Doubly excited configuration; not a pure spin state
G	N	0	0, 1	Highly excited configuration; not a pure spin state
H	$N+1$	$\frac{1}{2}$	$\frac{1}{2}$	Ground configuration of the $N+1$ electron system
I	$N+1$	$\frac{1}{2}$	$\frac{1}{2}$	Excited configuration of the $N+1$ electron system
J	$N+1$	$\frac{1}{2}$	$\frac{3}{2}$, $\frac{1}{2}$	Excited configuration of the $N+1$ electron system; does not correspond to pure spin state; enters both quartet and doublet states
K	$N-1$	$\frac{1}{2}$	$\frac{1}{2}$	Ground configuration of the $N-1$ electron system; doublet state; Koopmans' configuration
L	$N-1$	$\frac{1}{2}$	$\frac{1}{2}$	Excited configuration of the $N-1$ electron system; doublet state; Koopmans' configuration
M	$N-1$	$\frac{1}{2}$	$\frac{3}{2}$, $\frac{1}{2}$	"Shake up" configuration; contains quartet and doublet states
N	$N-1$	$\frac{3}{2}$	$\frac{3}{2}$	"Shake up" configuration; pure quartet state
O	$N-1$	$\frac{1}{2}$	$\frac{1}{2}$	"Core-ionized" configuration; doublet state
P	$N-1$	$\frac{1}{2}$	$\frac{3}{2}$, $\frac{1}{2}$	"Shake up" configuration connected with core ionization; enters both quartet and doublet states
Q	$N-2$	0	1, 0	Valence "shake off" configuration; not a pure spin state
R	$N-2$	1	1	Core "shake off" configuration; triplet state

example, the acronym PES stands for photoelectron spectroscopy; UPS and XPS for UV and x-ray induced photoelectron spectroscopy, respectively; and ESCA for electron spectroscopy for chemical analysis. XPS and ESCA are the same techniques. The acronym ESCA is quite misleading in that the technique has a much wider range of applicability than this name implies. The acronyms PES and UPS are often used interchangeably, although PES is usually considered to embrace both UPS and XPS. The term "electron spectroscopy" describes a technique in which the kinetic energies and fluxes of electrons are measured; the word "photoelectron" relates to the creation of electrons by photons; and the letters, "U" and "X" refer to the energies (i.e., UV or x-ray) of the exciting photons. Although this terminology may be confusing, its use is quite precise. In the same, somewhat-arbitrary fashion we reserve the term "excitation" for bound → bound transitions, the term "ionization" for bound → unbound transitions, and the term "transition" for both excitation and ionization.

The terms "shake-up" and "shake-off" originated in photoelectron spectroscopy and are quite graphic. Photon excitation of an atom or molecule may cause ionization of one electron and leave the system so disturbed (in the vernacular: so "shook up")

TABLE V. Photoinduced Electron Transitions

Confign excitation	Name of transition	Name of exptl process	Pictorial process of Fig 3
A → B, C, D, E, F	Electronic excitation	VIS/UV absorption spectroscopy	1
A → G	Core excitation	X-ray absorption spectroscopy	2
B → A	Phosphorescence	Emission spectroscopy	7
^{1}C → A	Fluorescence		
B → ^{3}E	Electronic excitation	Triplet-triplet absorption	
H → A, B	Ionization of the $N + 1$ electron system		
A → K, . . . , R	Ionization	Photoelectron spectroscopy	3, 4
A → M, N, P	"Shake-up"	Photoionization	5
A → Q, R	"Shake off"		6
(A→) O → Q	Auger transition	Auger spectroscopy	9
(A→) E → K	Autoionization		8
(A→) O → K	X-ray emission	X-ray emission spectroscopy	10

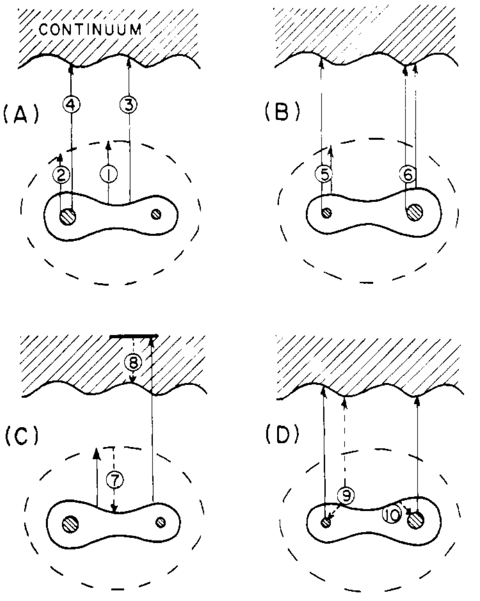


Figure 3. Pictorial representation of different transitions: (A) contains "simple" events; (B) contains simultaneous events; (C) and (D) contain consecutive events.

that another electron may suffer excitation (i.e., "shake-up") or even ionization (i.e., "shake-off"). These "shake-up/shake-off" processes are concurrent, not consecutive.

One limitation of Figure 2 is already evident: the configurations C, D, E, F, G, J, M, P, and Q do not represent pure spin states. All of these configurations participate in at least two state functions between which $\Delta S = 1$. This difficulty characterizes open-shell systems. A correct spin permutation symmetry requires that more than one determinant be used to describe most open-shell electronic states.

2. Transition Probabilities

If the orbital set of Figure 2 is identical for all configurations, certain selection rules will govern transition probabilities. For example, if the transition $\psi_a \rightarrow \psi_b$ is electric dipole allowed, the transition moment $\langle \psi_a | \Sigma \mathbf{r}_i | \psi_b \rangle$ must differ from zero. Since $\mathbf{r}_i$ is a one-electron operator, nonzero values of $\langle \psi_a \cdot | \Sigma_i \mathbf{r}_i | \psi_b \rangle$ can arise only when the two determinants ψ_a and ψ_b differ by no more than one spin orbital (cf. Table III). Thus, the optical transitions A → ^{1}C, ^{1}D, ^{1}E, ^{1}G, K, L, and O are allowed, in the absence of space-symmetry inhibitions, by the Slater rules. The optical transitions A → ^{1}F, ^{2}M, ^{2}N, and ^{2}P, on the other hand, are forbidden by the same rules. If these latter transitions occur at all, their intensity must be "stolen" by configuration interaction. For example, the transition A → ^{1}F could acquire intensity by a mixing of ^{1}F with any or all of ^{1}C, ^{1}D, ^{1}E, or ^{1}G. The transitions A → ^{4}M, ^{4}N, Q, and R are also forbidden; however, they can obtain intensity by mixing with continuum orbitals or by spin-orbit coupling. The optical transitions A → B, ^{3}C, ^{3}D, ^{3}E, and ^{3}G are also electric-dipole forbidden but may acquire intensity by spin-orbit coupling.

The experimental counterparts of the forbidden processes described above do occur. Therefore, in an experimental sense, they are "allowed". This allowedness is a consequence of the fact that our description of all states, A to R, by configurations constructed from a single set of orbitals is inadequate. Nonetheless, the theoretical distinction between forbidden and allowed processes is one which holds up well in practice, in other words, even when observed, these "forbidden" events are weak. Thus, the theoretical distinctions are empirically useful.

3. Less Familiar Processes

Some comment on the less-familiar processes of Tables IV and V is in order.

1. Distinctions between *direct* and *consecutive* processes are feasible.

(a) The event (A →)D → L is an autoionization, and it consists of two consecutive processes. The event A → L is a simple direct ionization event. Although the energies of the emitted electrons, ionized and autoionized, are equal in both instances, the actual band shapes, flux vs. energy, may be very different. Direct ionization is characteristic of the geometry of A. Autoionization, however, is characteristic of the geometry of D. In other words, the intermediate state D, having a lifetime of the order of a few vibrational periods, relaxes from a geometry characteristic of A to one more nearly characteristic of its own equilibrium requirements before it releases an electron into the continuum.

(b) The event (A →)O → Q is an Auger transition. It is a consecutive event, in contrast to the "shake-off" event A → Q which is a direct event. Both processes, Auger and "shake-off", involve the same two terminal and initial states, Q and A. The "shake-off" process (i.e., the direct ejection of two electrons) involves two initial particles, one being a photon, and three final particles. Given that the kinetic energy of the doubly ionized atom or molecule is small because of the large system inertia, it follows that the sum of energies of the two ejected electrons is $E(1 + 2) = h\nu - (E_Q - E_A)$. Consequently, the energy of either one of these two electrons is continuously variable within the limits $0 \leq E(1 \text{ or } 2) \leq h\nu - (E_Q - E_A)$. The energy of an Auger electron, on the other hand, is quite precise, is given by $E_Q - E_O$, and is independent of the input photon energy.

2. X-ray and Auger emission processes are competitive. The relative probability of the x-ray process increases with atomic number.

3. Transitions which initiate in a state other than the ground state require a fairly high population of this initial state. Such experiments are difficult to perform. With the advent of laser technology, they will shortly become quite common. On the other

hand, consecutive excitation/deexcitation events are easily observed. Most of the commonly observed processes (e.g., fluorescence, phosphorescence, autoionization, Auger events, X-ray emission, etc.) fall in this latter category.

4. Limitations

It is obvious that the classification schemes of Tables IV and V and Figures 1, 2, and 3 do not arise from the MO approximation. In fact, these classification schemes impose another, distinct approximation: they imply that one set of orbitals suffices for the various states. There are three different aspects to this approximation.

The first is practical. It asks whether or not the classification schemes work.

The second deals with numerical accuracy. It enquires into the correspondence between experiment and theory which can be achieved using a single determinantal wave function and only one set of orbitals.

The third is purely theoretical. It is concerned with the conditions under which these approximations can be embedded in or justified by theory.

The first question is easily answered; these classification schemes are exceedingly useful. In fact, in some form or other, they provide the basis for almost all spectroscopic discussions. The answer to the second question is equally clear; although the numerical agreement between quantities calculated on the MO level and their experimental counterparts may be imperfect, the MO description holds fairly well, especially for the ground state and for "normal" bond distances.[20] The third question is the most difficult, and it is the one on which we will concentrate; section II will deal mainly, but not exclusively, with the interrelations of the different electronic states of one given molecule or atom, whereas the emphasis in section III will devolve on the relationships of the electronic states of a composite molecule to the electronic states of its constituent parts. The central motif of section II is Koopmans' theorem, which invests the canonical orbitals with a physical significance distinct from that of all other Hartree–Fock orbitals. The essence of section III is an effort to provide a unifying approach to the diverse types of "orbital interactions" which have been invoked, usually in ad hoc fashion, to "explain" this or that type of experimental result.

II. Koopmans' Considerations

A. Valence Orbitals

The distinction between valence orbitals and core orbitals is valid in both experimental and theoretical senses.

On the experimental side, the photon energies required to ionize a core electron are considerably larger than those required to ionize valence electrons (see Table I). The larger photon energies and the ancillary instrumental demands for better vacuum, better analysis, and better detection technologies have caused the apparatus for core studies to deviate markedly from that for valence studies.

On the theoretical side, the removal of a core electron is a considerably larger and very different perturbation than that caused by removing a valence electron. For example, the removal of a C 1s electron of CH_4, as is discussed in section II.C.2.b, yields a CH_4^+ ion which is essentially identical with a ground state NH_4^+ ion; specifically, removal of a C 1s electron is equivalent to increasing the effective nuclear charge of carbon by one unit. It is difficult, on the other hand, to imagine any valence ionization process capable of generating a CH_4^+ entity which is remotely similar to any state of an ammonium ion. The point of relevance, of course, is that many of the concepts which are useful in UPS studies may well be useless in XPS studies, and vice versa.

1. Valence Ionization

The UPS study of valence ionizations has generated a wealth of evidence in favor of the MO approximation.[21] Indeed, the evidential tilt is so overwhelming that one tends to forget that the MO approximation is, in fact, an approximation at all. For this reason, we intend to derive Koopmans' theorem,[22] outline its approximational content, and discuss it in relation to photoelectron spectroscopy.

a. Koopmans' Theorem: First Part

We describe the ground state of an *N*-electron system in the MO approximation by

$$\Psi_0^N = \psi_0^N = |\varphi_a(1)\varphi_b(2)\ldots\varphi_n(N)| \tag{35}$$

We also approximate the cationic state obtained in a particular ionization process, Ψ_{-n}^{N-1}, by a single Slater determinant. Finally, we impose the restriction that Ψ_0^N and Ψ_{-n}^{N-1} be fabricated from an identical set of spin orbitals. Consequently, we write

$$\Psi_{-n}^{N-1} = \psi_{-n}^{N-1} = |\varphi_a(1)\varphi_b(2)\ldots\varphi_m(N-1)| \tag{36}$$

Under these conditions, the ionization energy equals the negative of the energy of the missing spin orbital

$$\mathrm{IE}_n = -\epsilon_{nn} \tag{37}$$

This statement constitutes the first part of Koopmans' theorem. Its proof follows directly from eq 15 and 22.

Proof: The ionization energy is given by

$$\mathrm{IE}_n = E(\psi_{-n}^{N-1}) - E(\psi_0^N) \tag{38}$$

where

$$E(\psi_{-n}^{N-1}) = \langle\psi_{-n}^{N-1}|\mathcal{H}^{N-1}|\psi_{-n}^{N-1}\rangle \tag{39}$$

$$\begin{aligned} = \sum_{\substack{k\in \mathrm{occ}\\ k\neq n}} \langle\varphi_k(1)|\mathcal{H}^{\mathrm{c}}(1)|\varphi_k(1)\rangle \\ + \sum_{\substack{k<l\in \mathrm{occ}\\ k,l\neq n}} \{\langle\varphi_k(1)\varphi_l(2)|1/r_{12}|\varphi_k(1)\varphi_l(2)\rangle \\ - \langle\varphi_k(1)\varphi_l(2)|1/r_{12}|\varphi_k(2)\varphi_l(1)\rangle\} \end{aligned} \tag{40}$$

and

$$E(\psi_0^N) = \langle\psi_0^N|\mathcal{H}^N|\psi_0^N\rangle \tag{41}$$

$$\begin{aligned} = \sum_{k\in \mathrm{occ}} \langle\varphi_k(1)|\mathcal{H}^{\mathrm{c}}(1)|\varphi_k(1)\rangle \\ + \sum_{k<l\in \mathrm{occ}} \{\langle\varphi_k(1)\varphi_l(2)|1/r_{12}|\varphi_k(1)\varphi_l(2)\rangle \\ - \langle\varphi_k(1)\varphi_l(2)|1/r_{12}|\varphi_k(2)\varphi_l(1)\rangle\} \end{aligned} \tag{42}$$

If we now multiply eq 22 from the left by ψ_n^* and integrate, we find

$$\langle\varphi_n(1)|\mathcal{F}(1)|\varphi_n(1)\rangle = \sum_l \epsilon_{nl}\langle\varphi_n(1)|\varphi_l(1)\rangle \tag{43}$$

$$= \epsilon_{nn} \tag{44}$$

where

$$\begin{aligned} \epsilon_{nn} = \langle\varphi_n(1)|\mathcal{H}^{\mathrm{c}}(1)|\varphi_n(1)\rangle \\ + \sum_{k\in \mathrm{occ}} \{\langle\varphi_n(1)\varphi_k(2)|1/r_{12}|\varphi_n(1)\varphi_k(2)\rangle \\ - \langle\varphi_n(1)\varphi_k(2)|1/r_{12}|\varphi_n(2)\varphi_k(1)\rangle\} \end{aligned} \tag{45}$$

The terms contained in eq 42 but not contained in eq 40 are identical with those of eq 45 but of opposite sign. Hence, it follows that

$$\mathrm{IE}_n = -\epsilon_{nn} \tag{46}$$

b. Koopmans' Theorem: Second Part[23]

Provided the set of spin orbitals $\{\varphi_k\}$ is the canonical Hartree–Fock set for the N-electron system, the negative of the orbital energy, $-\epsilon_n$, is the best ionization energy. If the word "best" means "best in a variational sense", this statement is the second part of Koopmans' theorem.

The $N-1$ electron wave function of the cation can be expanded over a set of determinants (i.e., a CI expansion for the cation states)

$$\Psi^{N-1} = \sum_{k\in \text{occ}} \psi_{-k}c_k + \sum_{\substack{k,l\in \text{occ}\\ \mu\notin \text{occ}}} \psi^{\mu}_{-kl}c^{\mu}_{kl} \tag{47}$$

where, for example, ψ^{μ}_{-kl} denotes a determinant from which the spin orbital φ_k has been deleted and in which φ_l has been replaced by φ_μ, and where we have dropped the $N-1$ superscript on ψ^{N-1} to avoid crowding.

Simplification of Ψ^{N-1} might consist of truncation to

$$\Psi^{N-1} = \sum_{k\in \text{occ}} \psi_{-k}c_k \tag{48}$$

However, what we really want is truncation to

$$\Psi^{N-1} = \psi_{-k} \tag{49}$$

This gross simplification of eq 47 to eq 49 is equivalent to the demand that we find an orthogonal transformation of the set of Hartree–Fock spin orbitals so that, simultaneously, the cationic state can be represented by one single determinant constituted from this set (i.e., eq 49) and the neutral molecule ground state can be represented by one single determinant constituted from the same set, namely by

$$\Psi_0^N = \psi_0 \tag{50}$$

Koopmans' theorem asserts this possibility and identifies the appropriate spin orbital set as the canonical Hartree–Fock set. The proof of these assertions follows:

Proof: If we can show that

$$\langle \psi_{-l}|\mathcal{H}^{N-1}|\psi_{-k}\rangle = 0,\ k \neq l \tag{51}$$

it follows that eq 49 represents the best variational approximation to eq 48. The proof of eq 51 proceeds in straightforward fashion. The Lagrangian multipliers ϵ_{kl} for a canonical set are zero when $k \neq l$. Consequently

$$\begin{aligned} 0 &= \langle \varphi_l(1)|\mathcal{F}(1)|\varphi_k(1)\rangle = \langle \varphi_l(1)|\mathcal{H}^c(1)|\varphi_k(1)\rangle \\ &+ \sum_{m\in \text{occ}} \{\langle \varphi_l(1)\varphi_m(2)|1/r_{12}|\varphi_k(1)\varphi_m(2)\rangle \\ &\quad - \langle \varphi_l(1)\varphi_m(2)|1/r_{12}|\varphi_k(2)\varphi_m(1)\rangle\} \qquad (52) \\ &= \langle \psi_{-l}|\mathcal{H}^{N-1}|\psi_{-k}\rangle \qquad (53) \end{aligned}$$

where the last step (i.e., eq 53) follows from Table III.

2. Electron Affinities

It may be shown, by a series of very similar approximations, that the "best" electron affinity is also given by

$$\text{EA}_\mu = -\epsilon_\mu \tag{54}$$

Since relatively little information is available for electron affinities,[24] we will concentrate here on ionization potentials.

3. Photoelectron Spectroscopy

The observables of photoelectron spectroscopy consist of the flux and energy of electrons emitted at a specific angle relative to the ionizing photon beam. These observables, after conversion to ionization cross sections and energies, are the quantities which must be related to theory.

The photoelectron spectrum of a typical molecule, ethylene, is shown on the right of Figure 4. It consists of a plot of electron flux vs. ionization energy. Each band corresponds to one electronic level of the ethylene cation. By Koopmans' theorem, the ionization energies can be approximated by negative orbital energies. Consequently, we also show, in the middle part of Figure 4 the result of an actual MO calculation. Two points are obvious. Firstly, all intense structures can be related to the removal of an electron out of an occupied orbital (i.e., "shake-up" processes are not very likely) and, secondly, the numerical agreement is better than 10%.

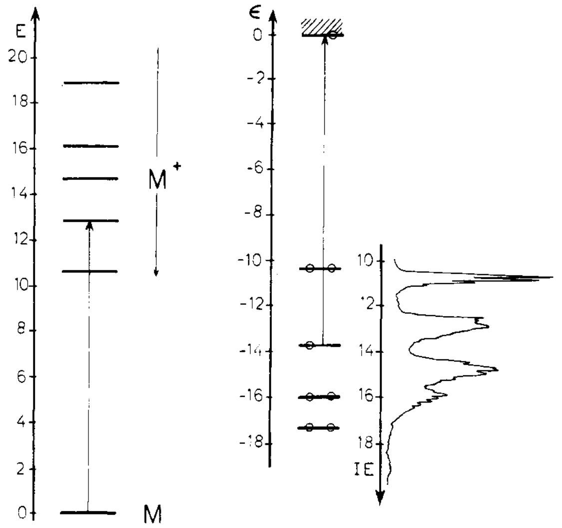


Figure 4. Energy levels of ethylene, neutral and cationic; orbital energies of neutral ethylene [C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, **94**, 1451 (1972)]; and the photoelectron spectrum of ethylene (ref 2a).

Koopmans' theorem provides a salient experiment/theory interface. Since we have gone to some trouble to "derive" it, and since its limits of validity are implicit in that derivation, we now outline these.

a. Fixed-Nuclei Approximation

It is the Born–Oppenheimer approximation which allows the notion of a "molecular geometry" (see section I.B.1). Thus, in addition to this approximation, it is also understood that the cationic $N-1$ electron system which is the immediately terminal state of the process

$$N\text{-electron system} + h\nu = (N-1)\text{-electron system} + e^-$$

is identical in all geometric detail with the initial state of the N-electron system. This, of course, is the Franck–Condon approximation. Consequently, Koopmans' theorem is pertinent only to vertical ionization events.

The vertical ionization energy,[25] which we denote IE_V, is usually taken to lie at the maximum of the cross section vs. IE plot (i.e , at the "top" of the photoelectron band). However, it is the 1st moment of this band, particularly if the band is either structured or skewed, which is the correct designation for IE_V.[25] In any event, IE_V must be distinguished from the adiabatic ionization energy, IE_A. The adiabatic ionization energy is the difference in energies of the vibrationally and rotationally unexcited states of the N- and $(N-1)$-electron systems.[85] Koopmans' theorem is not valid for IE_A, unless $\text{IE}_\text{A} = \text{IE}_\text{V}$. The distinction between IE_A and IE_V is shown in Figure 5.

b. Correlation Energy

The neglect of correlation energy is intrinsic to the Hartree–Fock approximation. The correlation energy is caused by the fact that electrons adjust their motions to the *instantaneous* charge distribution, and not to an *average* charge distribution (as is assumed in the Hartree–Fock equations). In fact, the correlation energy is the difference between the correct energy and the Hartree–Fock energy associated with any given Hamiltonian operator. If relativistic effects are small, the latter is well known, and the "correct energy" is equivalent to the experimental energy.

Electrons of opposite spin will usually tend to stay considerably further apart (i.e., correlate their motions better) than a single determinantal wave function will allow. Thus, the correlation energy can be quite substantial. Nonetheless, while large for any one state, it is only the difference of that between two states, namely, that between the initial *N*- and terminal (*N* − 1)-electron states, which is of significance to photoelectron spectroscopy. This difference may well be small. Koopmans' theorem implies that it is zero.

c. Relaxation Energy

The same set of spin orbitals is used to construct the Slater determinants for the *N*- and (*N* − 1)-electron systems. This supposition implies that the electrons of the cation do not adjust in any way to the reduction of interelectronic repulsions which must characterize the (*N* − 1)-electron system. This supposition is known as the "frozen-core" or "frozen-orbital" approximation.

d. Nonrelativistic Approximation

This approximation is not a consequence of the functional nature of the wave functions; it is, rather, a defect caused by the omission of relativistic terms from the Hamiltonian operator. We have omitted these terms solely for convenience. The various relativistic terms, for example, spin–orbit or spin–spin interactions, might have been included in the Fock operator in a way which would not have altered any of our prior conclusions. In fact, in his original paper,[22] Koopmans included relativistic effects explicitly,[26] and to no ill effects whatsoever in the form of eq 37.

e. Restriction to Closed-Shell Systems

Koopmans' theorem is restricted to closed-shell *N*-electron systems. Thus, at least in the form expressed here, it is specifically inapplicable to non-closed-shell systems (e.g., many transition metal complexes).

Koopmans' theorem is also restricted to certain *N* − 1 electron cationic states. These are referred[27] to as "Koopmans' configurations". For example, the configurations K, L, and O of Figure 2 are Koopmans' configurations, whereas the "shake-up" configurations M, N, and P are not. Ionizations of the ground state which terminate on a "shake-up" configuration are electric-dipole forbidden. Such "shake-up" transitions, if observed at all, usually have very low cross sections.

4. Critique of Koopmans' Theorem

a. Energies

Koopmans' theorem, when applied to MO calculations, is a means of computing approximate IE_V's. The reasonableness of the approximations involved is a matter of taste. The errors in a MO calculation may amount to 1–3 eV. Such errors are large relative to the magnitudes of IE_V's as obtained by UPS. Nonetheless, relative to the total electronic energies of a moderately small molecule, which may amount to thousands of electron volts, such an error is quite small.

However, a 1–3-eV error range is crucial to the assignment of UPS ionization energies. Thus, it is dangerous to attempt the assignment of cationic states which differ by less than 1 eV. As confirmation of this cautionary note, we emphasize three points.

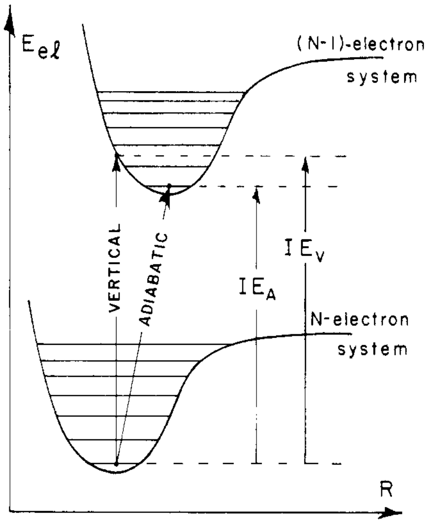


Figure 5. The vertical and adiabatic processes for the ionization event *N*-electron system + $h\nu$ = (*N* − 1)-electron system + e^-.

(1) Several breakdowns of Koopmans' theorem are known. That is, there exist systems where the sequence of cationic states differs from the sequence of canonical orbitals.

(2) The known breakdowns are few. However, if one considers the information needed to verify such a breakdown, one rapidly concludes that such breakdowns might be more common than not. The information required[28] involves good Hartree–Fock calculations as well as calculations which extend beyond the limitations of the Hartree–Fock approach and/or an experimental assignment of the cationic states. All of these are difficult to obtain. Hence, the widespread conclusion that the sequence of canonical orbitals matches that of the cationic states is more the result of a dearth of contradictory evidence than of any actual confirmatory data. Nonetheless, the existence of certain empirical relations, for example[29]

$$IE_k = -0.92\epsilon_k \qquad (55)$$

implies just such a matching of the two sequences.

(3) The validity of Koopmans' theorem does not hinge on the use of Hartree–Fock orbitals. However, it makes no sense to discuss the validity of the approximations inherent to Koopmans' theorem within the context of computational schemes which are of lower quality than Hartree–Fock. Indeed, the much-parametrized quantum chemical computational schemes (e.g., SPINDO[30]) should be viewed as prescriptions for the calculation of IE's, rather than as MO calculations.

Molecular orbital energies, as obtained by the CNDO/2 algorithm, are plotted vs. experimental ionization energies in Figure 6. This particular plot, which is probably quite representative of the general quality of such correlations, is impressive. The least-squares fit is $\epsilon = -1.33IE_V + 1.53$ and the standard deviation is $\sigma = 0.5$ eV.

b. Intensities

Koopmans' theorem is also an approximate selection rule for photoelectron spectroscopy. This facet of the theorem has been touched on previously, and it probably is its most important content. If Koopmans' theorem were exact, only transitions

$$\psi_0 \rightarrow \psi_{-k} \qquad (56)$$

would be allowed, whereas all "shake-up" (removal of one electron and excitation of another) and "shake-off" (double ionization) transitions would be forbidden. This is the aspect of Koopmans' theorem which is best supported by experiment and computation and which, in turn, provides the best buttressing for the extensive use of poor-quality, semiempirical calculations.

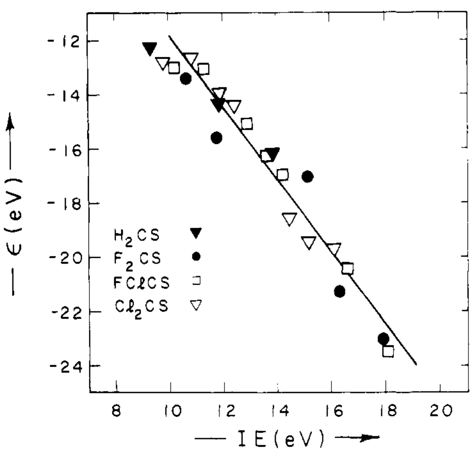


Figure 6. A correlation of vertical ionization energies IE_V and CNDO/2 orbital energies for H_2CS, F_2CS, FClCS, and Cl_2CS. The data used are taken from K. Wittel, Ph.D. Dissertation, Frankfurt (W. Germany), 1974; K. Wittel, A. Haas, and H. Bock, *Chem. Ber.*, **105,** 3865 (1972); H. W. Kroto and R. J. Suffolk, *Chem. Phys. Lett.*, **15,** 545 (1972); and B. Solouki, P. Rosmus, and H. Bock, *J. Am. Chem. Soc.*, **98,** 6054 (1976). The standard deviation is comparable to certain differences of ionization energy which occur in the PES of Cl_2CS (i.e., the chlorine lone-pair ionization events) and, as a result, these assignments are doubtful.

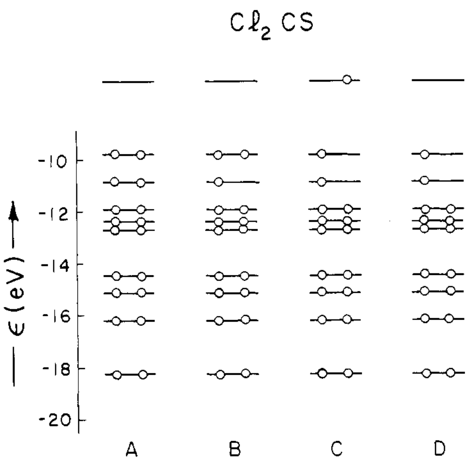


Figure 7. Electronic configurations of thiophosgene, Cl_2CS: (A) the ground state, (B) a Koopmans' configuration, (C) a shake-up, and (D) a shake-off configuration. Note that (A) refers to *N*-, (B) and (C) to (*N* − 1)-, and (D) to (*N* − 2)-electron systems. (A) is drawn using the experimental ionization energies *and* Koopmans' theorem; hence, the energies are MO energies.

"Shake-up" transitions, which have zero probability within the Koopmans' context, are often observed, particularly in conjunction with core ionizations. Usually, they are of low cross section. If they are of high intensity, it is probable that, in this instance, the equality $IE_k = -\epsilon_k$ is invalid. Conversely, when it is known that $IE_k = -\epsilon_k$ is a poor equality, it might be expected that "shake-up" transitions $\psi_0 \rightarrow \psi^{\mu}_{-kl}$ should also be relatively intense.

Different configurations of thiophosgene, Cl_2CS, are shown in Figure 7. Transitions from the ground configuration (A) to Koopmans' configurations (B) are allowed and account for all the major structures in the photoelectron spectrum of Figure 8. Transitions to the "shake-up" (C) and "shake-off" (D) configurations, if they occur at all, contribute only to the weak background beyond 15 eV. A rough estimate of "shake-up" transition energies is obtained by adding ionization energies to ultraviolet excitation energies, yielding a lower limit of ~14 eV. By a similar argument, "shake-off" energies should exhibit a lower limit of ~21 eV. The one-to-one correspondence between the number of photoelectron bands and the number of orbitals (in other words, the validity of the selection rule aspects of Koopmans' theorem) is not founded on theory, but on the experience gleaned from a great deal of experimental work.

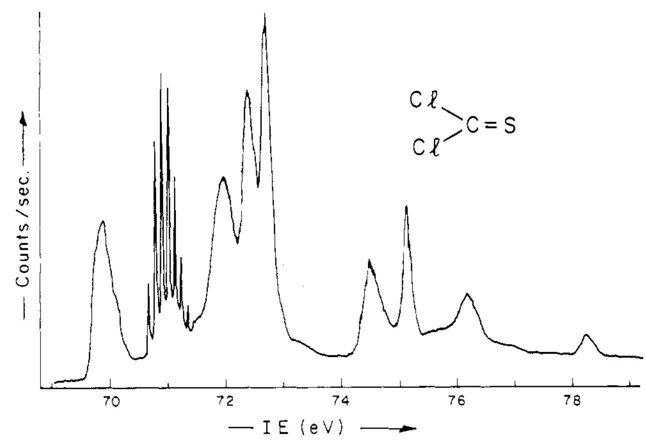


Figure 8. The photoelectron spectrum of Cl_2CS. The intensity scale is linear.

c. Uniqueness of the Canonical Set

Photoelectron spectroscopy, by virtue of its constant referral to Koopmans' theorem, has enhanced the credibility of the MO concept. It has attached a quality of an "observable" to the canonical MO energy and, thereby, has intensified the use of MO concepts in all of chemistry. Unfortunately, it is often forgotten that ψ_k and ϵ_k have direct experimental significances only for ionization events. In fact, the set of canonical MO's, although uniquely defined in a mathematical sense, is totally arbitrary. Localized MO's, for example, are heavily exploited in chemistry because of their transferability from molecule to molecule and because they are more closely connected with traditional chemical ideas concerning homology and reactive groupings. Indeed, any set of MO's which is obtained from the canonical set by a linear transformation of this set is equally as good as the canonical set itself. Thus, the pertinent set of orbitals depends on taste and may be canonical (usually delocalized), localized, or otherwise; the only requirement is that the *total* electron distribution remain unaltered. Koopmans' theorem, however, invests the canonical set with a certain uniqueness for ionization events. And it is this investiture, coupled with the accessibility of PES data, which makes Koopmans' theorem so important.

5. Valence Excitation

Having established a description of ionization events as a removal of electrons from specific orbitals, we now wish to investigate whether valence excitations can be described as

$$\varphi_k \rightarrow \varphi_\mu \tag{57}$$

It turns out that they cannot; permutational and space symmetry requirements force a departure from the single-determinant description of electronic states (i.e., from the MO approximation).

a. Nonexistence of a "Koopmans' Theorem" for Electronic Excitations

We use the same approximations as previously. These are

$$\Psi_0 = \left|\varphi_a(1)\varphi_b(2)\ldots\varphi_k\ldots\varphi_n(N)\right| = \psi_0 \tag{58}$$

$$\Psi_k^\mu = \left|\varphi_a(1)\varphi_b(2)\ldots\varphi_\mu\ldots\varphi_n(N)\right| = \psi_k^\mu \tag{59}$$

The excitation energy ΔE_k^μ is given by

$$\Delta E_k^\mu = \epsilon_\mu - \epsilon_k - J_{k\mu} + K_{k\mu} \tag{60}$$

where $J_{k\mu}$ and $K_{k\mu}$ are coulomb and exchange integrals, respectively, and are given by

TABLE VI

A. Configuration Wave Functions (One-Electron Excitations Only)

Configuration	Wave function
ψ_0	$\lvert\phi_a\alpha\phi_a\beta\phi_b\alpha\phi_b\beta \ldots \phi_k\alpha\phi_k\beta \ldots \phi_n\alpha\phi_n\beta\rvert$
$\psi_{k\alpha}^{\mu\alpha}$	$\lvert\phi_a\alpha\phi_a\beta\phi_b\alpha\phi_b\beta \ldots \phi_\mu\alpha\phi_k\beta \ldots \phi_n\alpha\phi_n\beta\rvert$
$\psi_{k\alpha}^{\mu\beta}$	$\lvert\phi_a\alpha\phi_a\beta\phi_b\alpha\phi_b\beta. \ldots \phi_\mu\beta\phi_k\beta \ldots \phi_n\alpha\phi_n\beta\rvert$
$\psi_{k\beta}^{\mu\alpha}$	$\lvert\phi_a\alpha\phi_a\beta\phi_b\alpha\phi_b\beta \ldots \phi_k\alpha\phi_\mu\alpha \ldots \phi_n\alpha\phi_n\beta\rvert$
$\psi_{k\beta}^{\mu\beta}$	$\lvert\phi_a\alpha\phi_a\beta\phi_b\alpha\phi_b\beta \ldots \phi_k\alpha\phi_\mu\beta \ldots \phi_n\alpha\phi_n\beta\rvert$

B. State Energies and Wave Functions (No Configuration Interaction)[a]

State	Wave function	M_S	S	$E(\Psi) - E(^1\Psi_0)$
$^1\Psi_0$	ψ_0	0	0	0
$^1\Psi$	$(\frac{1}{2})^{1/2}(\psi_{k\alpha}^{\mu\alpha} + \psi_{k\beta}^{\mu\beta})$	0	0	$\epsilon_\mu - \epsilon_k - J'_{k\mu} + 2K'_{k\mu}$
$^3\Psi$	$\psi_{k\beta}^{\mu\alpha}$	1	1	$\epsilon_\mu - \epsilon_k - J'_{k\mu}$
$^3\psi$	$(\frac{1}{2})^{1/2}(\psi_{k\alpha}^{\mu\alpha} - \psi_{k\beta}^{\mu\beta})$	0	1	
$^3\Psi$	$\psi_{k\alpha}^{\mu\beta}$	−1	1	

[a] J' and K' are defined in terms of *space orbitals*. Thus $J'_{k\mu} = \int\int \phi_k{}^*(1)\phi_\mu{}^*(2)[1/r_{12}]\phi_k(1)\phi_\mu(2)\, dr_1dr_2$ and $K'_{k\mu} = \int\int \phi_k{}^*(1)\phi_\mu{}^*(2)[1/r_{12}]\phi_k(2)\phi_\mu(1)\, dr_1dr_2$.

$$J_{k\mu} = \langle \varphi_k(1)\varphi_\mu(2) | 1/r_{12} | \varphi_k(1)\varphi_\mu(2)\rangle \qquad (61)$$

$$K_{k\mu} = \langle \varphi_k(1)\varphi_\mu(2) | 1/r_{12} | \varphi_k(2)\varphi_\mu(1)\rangle \qquad (62)$$

The derivation of eq 60 is straightforward and is not given here. Instead, we merely ask if eq 60 is the "best" approximation to the excitation energy, and we enquire whether or not the use of the canonical set is better in any way than any other set. If ΔE_k^μ of eq 60 were "best", then it follows that no two excited configurations, ψ_k^μ and ψ_l^ν, could interact, that is, that $\langle\psi_k^\mu|\mathcal{H}^N|\psi_l^\nu\rangle = 0$. This, of course, is not the case. The use of the Slater rules of Table III leads to

$$\begin{aligned}\langle\psi_k^\mu|\mathcal{H}^N|\psi_l^\nu\rangle = {} & \langle\varphi_\mu(1)\varphi_l(2)|1/r_{12}|\varphi_k(1)\varphi_\nu(2)\rangle \\ & - \langle\varphi_\mu(1)\varphi_l(2)|1/r_{12}|\varphi_k(2)\varphi_\nu(1)\rangle \neq 0 \qquad (63)\end{aligned}$$

Two points emerge from all of this. Firstly, although eq 60 does contain orbital energies, the excitation energy is not simply equal to their difference.[31] And secondly, in contrast to the minimum property of Koopmans' configurations, the expression of eq 60 is inadequate.

The above inadequacies are intrinsic to the definition of the Fock operator

$$\mathcal{F}^N(1) = \mathcal{H}^c(1) + \sum_{l \in \text{occ}} \int d\mathbf{x}_2 \cdot \varphi_l{}^*(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_l(2) \qquad (23')$$

were the summation runs over all orbitals which are occupied in the ground configuration. When $\mathcal{F}^N(1)$ acts on an orbital l' which is occupied in ψ_0, the electron interaction for one of the terms of eq 23′ is zero in the sense that

$$\begin{aligned}\int\int d\mathbf{x}_1 d\mathbf{x}_2 \cdot \varphi_{l'}{}^*(1)\varphi_{l'}{}^*(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_{l'}(1)\varphi_{l'}(2) \\ = \langle\varphi_{l'}(1)\varphi_{l'}(2)|1/r_{12}|\varphi_{l'}(1)\varphi_{l'}(2)\rangle \\ - \langle\varphi_{l'}(1)\varphi_{l'}(2)|1/r_{12}|\varphi_{l'}(2)\varphi_{l'}(1)\rangle = 0 \qquad (64)\end{aligned}$$

As a result, we say that the Fock operator excludes electron self-interactions and allows the electron under study, if it be in one of the spin orbitals of ψ_0, to interact only with the other $(N - 1)$ electrons in ψ_0. However, when $\mathcal{F}^N(1)$ acts on an orbital which is not contained in ψ_0, say φ_μ where $\mu \notin$ occ, all terms of the summation of eq 23′ are nonzero. Thus, the energy of the virtual (unoccupied) spin orbital refers to an $(N + 1)$-electron system. Or, somewhat equivalently, the spin orbital φ_μ describes the motion of an electron in the field produced by the nuclei and by N other electrons. The integrals $J_{k\mu}$ and $K_{k\mu}$ of eq 60 remedy this very artificial situation by deleting the unnecessary terms of ϵ_μ from ΔE_k^μ. It is for this same reason that the virtual canonical orbitals are not optimal for excited states (i.e., are responsible for the CI property demanded by eq 63).

TABLE VII. Singlet-Triplet Splitting in Representative Molecules[a]

Molecule	Excitation type	$E(S) - E(T)$ (cm^{-1})
H_2CO	n → π^*	2 996
Cl_2CS	n → π^*	2 500
Pyrazine	n → π^*	4 050
Pyrimidine	n → π^*	2 630
Benzene	$\pi \rightarrow \pi^*$	18 580
Naphthalene	$\pi \rightarrow \pi^*(L_a)$	13 354
Hexahelicene	$\pi \rightarrow \pi^*(L_a)$	8 100

[a] These data are taken from S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969.

b. Spin Multiplicity

When relativistic effects are small, we may write the spin orbitals as

$$\begin{aligned}\varphi_k(\mathbf{x}_1) = \varphi_k(\mathbf{r}_1,\omega_1) = \phi_k(\mathbf{r}_1)\alpha(\omega_1) \\ \varphi_{k'}(\mathbf{x}_1) = \varphi_{k'}(\mathbf{r}_1,\omega_1) = \phi_k(\mathbf{r}_1)\beta(\omega_1)\end{aligned} \qquad (65)$$

As a result, any configuration φ_k^μ is fourfold degenerate in the sense that the $\psi_0 \rightarrow \psi_k^\mu$ excitation can be written in four ways

$$\begin{aligned} \phi_k^\alpha &\rightarrow \phi_\mu^\alpha & M_S &= 0 \\ \phi_k^\alpha &\rightarrow \phi_\mu^\beta & M_S &= -1 \\ \phi_k^\beta &\rightarrow \phi_\mu^\alpha & M_S &= 1 \\ \phi_k^\beta &\rightarrow \phi_\mu^\beta & M_S &= 0 \end{aligned} \qquad (66)$$

all of which contain the same space orbital promotion. As indicated, the excited configurations differ in their spin quantum number M_S. The $M_S = \pm 1$ configurations are two components of a triplet state (i.e., a state for which $S = 1$). The ±1 components are pure spin states (i.e., the single determinants $\psi_{k\alpha}^{\mu\beta}$ and $\psi_{k\beta}^{\mu\alpha}$ are simultaneous eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}_z$). The single Slater determinants $\psi_{k\alpha}^{\mu\alpha}$ and $\psi_{k\beta}^{\mu\beta}$, on the other hand, are not pure spin states. In order to obtain simultaneous eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}_z$, we are forced to write

$$\begin{aligned} (\tfrac{1}{2})^{1/2}\{\psi_{k\alpha}^{\mu\alpha} + \psi_{k\beta}^{\mu\beta}\} \qquad & M_S = 0,\ S = 0 \\ (\tfrac{1}{2})^{1/2}\{\psi_{k\alpha}^{\mu\alpha} - \psi_{k\beta}^{\mu\beta}\} \qquad & M_S = 0,\ S = 1 \end{aligned} \qquad (67)$$

where the upper is the singlet state and the lower is the $M_S = 0$ component of the triplet state. The energies of the singlet and triplet states are given in Table VI. The three triplet components remain degenerate in the absence of spin-orbit or spin–spin coupling.

The energy differences between singlet and corresponding triplet states may be quite large, as is demonstrated in Table VII. In a simplistic approach, this singlet/triplet splitting equals twice the exchange integral $K_{k\mu}$, showing that this integral is far from negligible.

Equations 67 demonstrate that spin orbital identities, in the sense of integral electron occupancy numbers, are irredeemably lost in certain excited states because of the spin-quantization demands. One could attempt to retain the concept of an average excitation energy for a $\phi_k \rightarrow \phi_\mu$ excitation by writing

$$\begin{aligned}\overline{\Delta E}_{k\rightarrow\mu} = {} & \tfrac{1}{4}[E(^1\psi) + E(^3\psi_1) + E(^3\psi_0) + E(^3\psi_{-1})] - E(^1\psi_0) \\ & = \epsilon_\mu - \epsilon_k - J'_{k\mu} + \tfrac{1}{2}K'_{k\mu} \qquad (68)\end{aligned}$$

The benefits of doing so are dubious: Once $J'_{k\mu}$ and $K'_{k\mu}$ are known, the energies of the component states are just as easily evaluated as is the average configurational energy defined by eq 68.

Singlet, triplet, etc., wave functions can be formulated without using the notion of electron spin at all. This circumstance does not change any prior conclusions. The multiplicity now refers to certain irreducible representations of the permutation group of all electrons. This topic has been discussed in detail by Matsen in an admirable series of papers on "spin-free" quantum chemistry.[32]

c. Degenerate Space Orbitals

When there is spatial degeneracy (e.g., $\pi \rightarrow \pi^*$ excitations in a linear molecule), the situation gets worse. The set of configurations $\{\psi_k^{\mu}, \psi_{k'}^{\mu'}, \psi_k^{\mu'}, \psi_{k'}^{\mu}\}$, where $\{k,k'\}$ and $\{\mu,\mu'\}$ indicate the degenerate components of π and π^*, respectively, spans a reducible representation of the molecular point group. In the general case, it is found that only certain linear combinations of the ψ_k^{μ}'s span irreducible representation spaces. Thus, a given electronic state must be described as a linear combination of two or more configurations. The net result is that the space orbital correspondence $\Psi_k^{\mu} \leftrightarrow k \rightarrow \mu$ is completely lost and that the energy expressions involve a variety of "exchange" integrals. In short, the MO description breaks down. The best known example for such a degeneracy is furnished by benzene, C_6H_6. The lowest π-orbital excitation ($e_{1g} \rightarrow e_{2u}$) yields three differents states of widely differing energies. These are: $^1B_{2u}$ (3.846 μm^{-1}), $^1B_{1u}$ (5.000 μm^{-1}) and $^1E_{1u}$ (5.405 μm^{-1}). This situation requires, at least, a superposition of configurations of the $\pi \rightarrow \pi^*$ ($e_{1g} \rightarrow e_{2u}$) type, as is provided within the Pariser–Parr–Pople framework.[3a]

Even in the case of near degeneracy, the interaction matrix elements of eq 63 can provide a very large mixing of different configurations. This fact is reflected in the failure of MO calculations to provide good estimates of excitation energies. Indeed, the inclusion of configuration interaction is a mandated requirement even when there is no obvious MO degeneracy or near-degeneracy.

d. A Consensus

The unpleasantness of the situation concerning excited electronic states, as delineated in sections II.A.5.a–c contrasts with the ease with which ionization events were handled in sections II.A.2–4. It is this disparity which accounts for the relatively simple manner in which photoelectron spectra may be interpreted—and, hence, the popularity of XPS and UPS—and the great difficulty attendant to any discussion of electronic absorption spectroscopy (i.e., VIS, UV, and VUV). We now enquire into ways in which these difficulties might be resolved.

1. One can perform HF-SCF calculations for certain excited states. However, this is a very difficult, very lengthy, and very expensive affair.

2. One might perform configuration interaction calculations using the ground-state orbital set. This is a routine procedure. However, for *n* occupied and *m* unoccupied orbitals there are *nm* singly excited configurations. Consequently, the task of truncating the very long CI expansion

$$\Psi = \psi_0 + \sum_{k,\mu} \psi_k^{\mu} a_k^{\mu} + \sum_{\substack{k,l\\ \mu,\nu}} \psi_{kl}^{\mu\nu} a_{kl}^{\mu\nu} + \ldots \qquad (69)$$

is troublesome, and this, coupled with the need for a proper choice of orbitals, requires a great deal of art and computer time. And, finally, the MO idea is totally lost in a long list of CI expansion coefficients.[33]

3. For a limited class of excitations, there exists an attractive alternative. If we confine attention to all the possible excitations of one spin orbital, say φ_m, we can construct a simple, modified orbital picture. We think that this modified approach is very powerful. As a result, we refer to these modified orbitals as "Optimum Excited State Orbitals", and we devote the next section to them.

6. *Optimum Orbitals for Excited Electronic States*

We will confine our interest to all excitations $\varphi_m \rightarrow \varphi_\mu$ where φ_m is some specific one of the orbitals contained in ψ_0, and φ_μ is any of the virtual set of eigenfunctions of $\mathcal{F}$. We now define the optimum excited orbitals[34] $\tilde{\varphi}_\mu$ by

$$\mathcal{F}_m(1)\tilde{\varphi}_\mu(1) = \tilde{\epsilon}_\mu \tilde{\varphi}_\mu(1) \qquad (70)$$

where $\mathcal{F}_m$ is the one-electron operator

$$\mathcal{F}_m(1) = \mathcal{H}^c(1) + \sum_{\substack{k \in occ\\ k \neq m}} \int d\mathbf{x}_2 \cdot \varphi_k^*(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_k(2) \qquad (71)$$

$$= \mathcal{F}(1) - \int d\mathbf{x}_2 \cdot \varphi_m^*(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_m(2) \qquad (72)$$

We also require that the virtual optimum orbital $\tilde{\varphi}_\mu$ be orthogonal to all those contained in ψ_0, namely that

$$\langle \tilde{\varphi}_\mu | \varphi_k \rangle = 0 \qquad k \in \text{occ} \qquad (73)$$

This condition is readily satisfied by expanding $\tilde{\varphi}_\mu$ in terms of the set of virtual Hartree–Fock orbitals of $\mathcal{F}$

$$\tilde{\varphi}_\mu = \sum_{\nu \notin occ} \varphi_\nu c_{\nu\mu} \qquad (74)$$

Given the expansion of eq 74, we can now write

$$\tilde{\psi}_m^{\mu} \equiv \psi_m^{\tilde{\mu}} = \sum_{\nu \notin occ} \psi_m^{\nu} c_{\nu\mu} \qquad (75)$$

and we can show that $\tilde{\psi}_m^{\mu}$ is optimum with respect to the *N*-electron Hamilton operator $\mathcal{H}^N$. The proof of this last statement requires that we show $\langle \tilde{\psi}_m^{\mu} | \mathcal{H}^N | \tilde{\psi}_m^{\lambda} \rangle = 0$ for $\mu \neq \lambda$. This requirement is demonstrated in eq 76–78.

$$\langle \tilde{\psi}_m^{\mu} | \mathcal{H}^N | \tilde{\psi}_m^{\lambda} \rangle = \langle \tilde{\varphi}_\mu(1) | \mathcal{H}^c(1) | \tilde{\varphi}_\lambda(1) \rangle + \sum_{\substack{k \in occ\\ k \neq m}} \langle \tilde{\varphi}_\mu(1)\varphi_k(2)[(1 - \mathcal{P}_{12})/r_{12}]\tilde{\varphi}_\lambda(1)\varphi_k(2) \rangle \qquad (76)$$

$$= \langle \tilde{\varphi}_\mu(1) | \mathcal{F}_m(1) | \tilde{\varphi}_\lambda(1) \rangle \qquad (77)$$

$$= 0 \qquad (78)$$

Equation 78 follows from the fact that $\tilde{\varphi}_\mu$ and $\tilde{\varphi}_\lambda$ are eigenfunctions of the same Hermitian operator, $\mathcal{F}_m$.

Excitation energies now consist of a difference of orbital energies

$$\Delta E_m^{\tilde{\mu}} = \langle \tilde{\psi}_m^{\mu} | \mathcal{H}^N | \tilde{\psi}_m^{\mu} \rangle - \langle \psi_0 | \mathcal{H}^N | \psi_0 \rangle \qquad (79)$$

$$= \langle \tilde{\varphi}_\mu(1) | \mathcal{H}^c(1) | \tilde{\varphi}_\mu(1) \rangle - \langle \varphi_m(1) | \mathcal{H}^c(1) | \varphi_m(1) \rangle + \sum_{\substack{k \in occ\\ k \neq m}} \langle \varphi_k(1)\tilde{\varphi}_\mu(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_k(1)\tilde{\varphi}_\mu(2) \rangle - \sum_{\substack{k \in occ\\ k \neq m}} \langle \varphi_k(1)\varphi_m(2)[(1 - \mathcal{P}_{12})/r_{12}]\varphi_k(1)\varphi_m(2) \rangle \qquad (80)$$

$$= \tilde{\epsilon}_\mu - \epsilon_m \qquad (81)$$

Thus, for each possible excitation of any *one* of the orbitals contained in ψ_0 (i.e., $\varphi_m \rightarrow$ any $\tilde{\varphi}_\mu$), we have constructed a set $\{\tilde{\varphi}_\mu\}$ which has all the nice properties of eq 78 and 81. Unfortunately, the set $\{\tilde{\varphi}_\mu\}$ is different for different choices of *m* and should be labeled accordingly, say as $\{\tilde{\varphi}_{\mu(m)}\}$. Furthermore, the orbitals from different sets need not be orthogonal (i.e., $\langle \tilde{\varphi}_{\mu(m)} | \tilde{\varphi}_{\nu(n)} \rangle \neq \delta_{\mu\nu}$).

For any one starting orbital, φ_m, the final orbitals $\tilde{\varphi}_\mu$ have several convenient properties: they are, by construction, orthogonal to all the occupied orbitals; they are eigenfunctions of a one-electron, effective Hamiltonian, $\mathcal{F}_m$, which corresponds to the ($N - 1$)- and not to the *N*-electron system; configurations constructed from the set $\{\tilde{\varphi}_{\mu(m)}\}$, say $\tilde{\psi}_m^{\nu}$, are noninteracting (i.e., the $\tilde{\varphi}_{\mu(m)}$ are optimal for the description of excited states which are generated by excitation of the spinorbital φ_m, $m \in$ occ); the

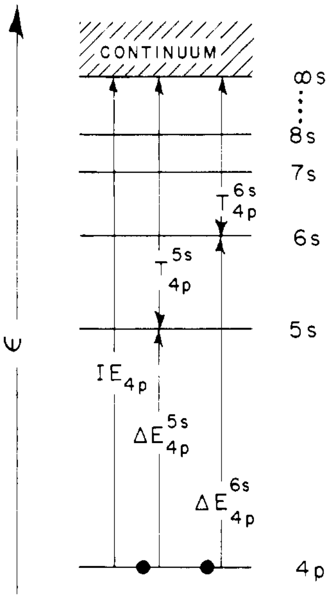


Figure 9. An example of a Rydberg series (schematic): The 4p → ns transitions of CH_3Br.

energy of $\psi_0 \rightarrow \tilde{\Psi}^{\mu}_{m}$ is given by orbital energy differences in eq 81.

This approach should be especially appropriate for molecules for which the first two ionization energies are widely separated. Under these conditions, one might expect that the excitation energies $\psi_0 \rightarrow \tilde{\psi}^{\mu}_{m}$ and $\psi_0 \rightarrow \tilde{\psi}^{\mu}_{n}$ should be quite different and, hence, that configuration interactions, such as $\langle \tilde{\psi}^{\mu}_{m} | \mathcal{H}^N | \tilde{\psi}^{\mu}_{n} \rangle$ might also be quite small. Thus, when $\langle \tilde{\psi}^{\mu}_{m} | \mathcal{H}^N | \tilde{\psi}^{\mu}_{n} \rangle \simeq 0$, an orbital description will be appropriate for all excitations $\varphi_m \rightarrow \tilde{\varphi}_{\mu}$, where m ($\in$ occ) is fixed and μ ($\notin$ occ) is variable. We suspect that these conditions are fulfilled for Rydberg states and we will discuss these in the next section.

B. Rydberg Orbitals[35]

Certain series of atomic and molecular electronic excitations obey the Rydberg formula

$$\Delta E = \mathrm{IE} - R/(n - \delta)^2 \qquad (82)$$

where ΔE is the transition energy; IE is the ionization energy; R is the Rydberg constant; n is the principal quantum number of the terminating orbital; and $\delta = \delta(l)$, the quantum defect, is a measure of the departure from simple hydrogen-like behavior. Such excitations are known as "Rydberg transitions".

The methyl bromide molecule, for example, exhibits a number of Rydberg series. The lowest ionization potential of CH_3Br is attributable to removal of an electron from an MO which is localized on the bromine center and of approximate 4p nature. In the progression toward the ionization limit, the 4p electron, as shown in Figure 9, may well be excited to any one of the 5s, 6s, 7s, . . . , ∞s orbitals of the bromine center. The excitations 4p → 5s, 4p → 6s, 4p → 7s, . . . 4p → ∞s (or IE_{4p}), which converge on the 4p ionization limit, constitute a Rydberg series. The actual situation may be a good deal more complicated than our simple example indicates: The VUV spectrum of CH_3Br, as shown in Figure 10, amply demonstrates this complexity.

The term value of an excited Rydberg level is

$$T_n = R/(n - \delta)^2 \qquad (83)$$

where n, in the specific case of CH_3Br, equals 5, 6, 7, . . . , ∞. This sort of behavior is reminiscent of an atom. In addition, one finds $\delta = \delta(l)$. For molecules in which the Rydberg chromophore is a 2*nd* row atom, it is found that[36]

$$\delta(\mathrm{s}) \simeq 1;\ \delta(\mathrm{p}) \simeq 0.6;\ \delta(\mathrm{d}) \simeq 0.1 \qquad (84)$$

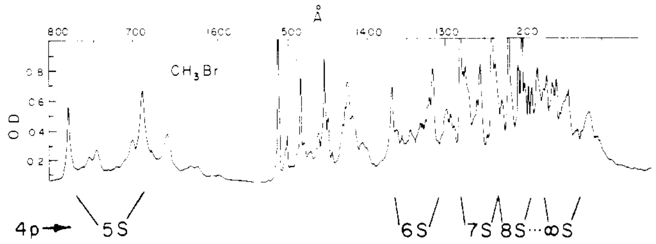


Figure 10. The VUV absorption spectrum of gaseous CH_3Br. The absorptive transitions 4p → 5s, 4p → 6s, etc., are indicated below the spectrum. The 4p → ∞s transition is an ionization event. The doubled nature of the Rydberg transitions is caused by spin–orbit coupling.

Thus, even in molecules, the value of δ is used to determine an "*l*-quantum number" for the Rydberg level. In other words, the empirical description of molecular Rydberg levels is, in essence, an atomic description.

This description agrees with our supposition that a Rydberg orbital is so large and so loosely bound as to be unaffected by the details of molecule architecture. In fact, one may suppose that the Rydberg electron of a neutral molecule "sees" a singly charged core which is almost spherically symmetrical and which it interpenetrates only very slightly. Indeed, one may guess the degree of penetration. Since, for given n, an s-type orbital is more penetrating than p which, in turn, is more penetrating than d, we might expect that deviation from hydrogen-like behavior would vary as s > p > d. This, as witness the values of $\delta(l)$, is precisely that which is observed.

The concept of "penetration" can be expressed differently. Any Rydberg orbital must be orthogonal to all core orbitals.[37] Thus, the Rydberg orbital with the largest core part is also the one with the greatest core-orthogonality requirements. Since the number of subshells of any readily conceivable core is s > p > d, orthogonality requires that the core parts of Rydberg vary as s > p > d. Thus, the core orthogonality requirement, which in turn devolves on the enumeration of core precursors, is merely another way of describing penetration.[38]

In any event, we arrive at the empirical conclusion that a Rydberg electron moves in a very large orbital, that it sees a more or less spherical core of unit charge which it deforms and/or penetrates slightly, and that the degree of deformation and/or penetration is larger for small n, and small l. Thus, we conclude that a Rydberg orbital is of the form

$$\varphi^{\mathrm{R}}_{nlm} \simeq R_{nl}(r) Y_{lm}(\theta,\phi) \qquad (85)$$

In accord with this, it is found that core/Rydberg exchange energies are small and that they decrease with increasing n and l.

We now propose, on the basis of the above suppositions, to "derive" the Rydberg equation.

1. Rydberg Equation

Inspection of Figure 9 indicates that the optimum virtual orbital approach of section II.A.6 should be particularly suited to a description of Rydberg series. Thus, for a Rydberg transition, we write

$$\Delta E^{\tilde{\mu}}_{m} = \tilde{\epsilon}_{\mu} - \epsilon_m \qquad (86)$$

Introducing Koopmans' theorem, this becomes

$$\Delta E^{\tilde{\mu}}_{m} = \mathrm{IE}_m + \tilde{\epsilon}_{\mu} \qquad (87)$$

Now according to eq 81, we have

$$\tilde{\epsilon}_{\mu} = \langle \tilde{\varphi}_{\mu}(1) | \mathcal{F}_m(1) | \tilde{\varphi}_{\mu} \rangle \qquad (88)$$

where the Fock operator $\mathcal{F}_m(1)$ is a one-electron effective Hamiltonian for an electron moving in the potential field of the nuclei and $N - 1$ other electrons. If the electron is far removed from this core, we may conclude that its primary effect on the

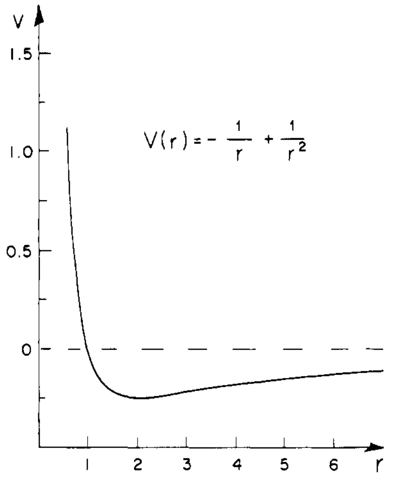


Figure 11. The potential $V(r_1) = -1/r + 1/r^2$.

core is to polarize it. Consequently, we suppose the Rydberg electron to move in the field of a polarizable core of unit charge.

For such a system, we write the potential part of $\mathcal{F}_m(1)$ as

$$V(1) = -1/r_1 + M/r_1^2 \tag{89}$$

where M is a constant. With this potential, the solutions to eq 70 are[39]

$$\tilde{\epsilon}_\mu = -R/[n_r + 1 + l + \delta_l]^2 \tag{90}$$

where $n_r = 0, 1, 2, \ldots$ is the radial quantum number, and δ_l is given by

$$\delta_l = [(l + \tfrac{1}{2})^2 + M]^{1/2} - l - \tfrac{1}{2} \tag{91}$$

$$\approx -M/(2l + 1) \tag{92}$$

Equation 90 for $\tilde{\epsilon}_\mu$ is of similar form to eq 83. The two forms can be made identical, in which case the relationship between δ_l of eq 91 or 92 and δ of eq 83 is readily obtained.

We now wish to make a comparison of theory and experiment. For this purpose, we choose the empirical synopsis of eq 84 for second-row atoms. We also choose the lowest energy s-Rydberg orbital in order to determine the value of M. Thus, with $n = 3$, we find the effective quantum number

$$n_l^* = n - \delta(l) \tag{93a}$$

to be 2 for the 3s Rydberg state. Since n_l^* is also given by

$$n_l^* = n_r + 1 + l + \delta_l \tag{93b}$$

we find, after insertion of $n_r = 0$, $l = 0$, and $n_l^* = 2$, that $\delta_l = 1$. From eq 91, it then follows that $M = 2$. Knowing M, we may calculate n_l^* for different l. These values of n_l^* are compared with the empirical values in Table VIII. The agreement is quite satisfactory. We conclude that eq 89 provides a fair description of the potential in which a Rydberg electron moves. This potential is sketched in Figure 11.

The solutions to eq 70, using the potential of eq 89 are given by the confluent hypergeometric functions

$$\tilde{\varphi}_\mu = \rho^{l'} e^{-\rho/2} F(n - l' - 1, 2l' + 2, \rho) Y_{l'm}(\theta,\phi) \tag{94}$$

These reduce to the hydrogenic functions for $M = 0$. Not surprisingly, we find the Rydberg orbitals to be of the form

$$\tilde{\varphi}_\mu = R(r) Y_{lm}(\theta,\phi) \tag{95}$$

Two final comments are required.

1. The approximation of eq 89 involves the replacement of the exchange term of $\mathcal{F}_m$ by an average local potential.[40] This approximation works only because core/Rydberg exchange energies are small. In fact, one could define a Rydberg orbital as one for which the exchange interactions with the core are negligible.

2. Since the Rydberg equation provides a good description of a great number of electronic transitions in atoms and in molecules, the approximation of eq 86 and 89 attain some measure of justification. Hence, we conclude that there is at least one class of electronically excited states which is amenable to a simple orbital treatment.

TABLE VIII. Effective Quantum Numbers Obtained from a Polarizable Core Model (Eq 89 with $M = 2$)

	n_l^*	
l	Expt (eq 84)	Theory (eq 91)
0	2	≡ 2
1	2.4	2.56
2	2.9	3.37

C. Core Orbitals

The core orbitals are discussed separately because the phenomena associated with them and the technology required for studying them are so different from those associated with valence electrons. Some of these differences are:

Core ionization and excitation require x-ray technology whereas valence ionization and excitation can usually be done with UV radiation.

Core ionization energies are characteristic of the atomic center from which ionization occurs. The effects of the other atomic centers in the molecule are normally so small, in a relative sense, that they can be discussed using perturbation theory. In fact, the effects of the neighboring atoms are supposedly diagnostic of the atomic environment and, as a result, the shifts of the core ionization energies from the free atom positions are known as "chemical shifts". These shifts are usually discussed using a point-charge potential model[41] (see section II.C.1.a).

Since the core orbital is localized on a specific atomic center, it follows, on the basis of an LCAO description of the valence orbitals, that intensities of core → valence excitations (i.e., x-ray absorption) in molecules can be discussed using atomic selection rules. This topic will be discussed in section II.C.2.a.

Koopmans' theorem does not hold nearly as well for core ionization events as for valence ionizations. For example, "shake-up" and "shake-off" events are more common for core ionization. This topic will be discussed in sections II.C.1.c, 2.b, and 3.

Core-ionized systems decay by emitting x-rays and/or Auger electrons. Valence-ionized systems exhibit a preference for a photochemical relaxation route. And, curiously enough, the x-ray and Auger relaxation channels appear to be the more heavily studied.

XPS has been extensively used for the study of solid materials.[42] The solid state contains many open-shell molecular systems, dominant among them being the transition metal compounds.[43] An open-shell N-electron system implies the possibility of a doubly open-shell ($N - 1$)-electron system. Such a situation can give rise to new phenomena. For example, exchange splittings of the cationic levels can be observed, and extensive "shake-up" associable with transitions of the types metal → metal, metal → ligand, ligand → metal, or ligand → ligand does occur. These phenomena cannot be described within the context of a simple orbital picture.

1. Core Ionizations

Core ionization energies are characteristic of the atom but do exhibit chemical shifts. These shifts reflect the influence of the neighboring atomic centers on the core orbital in question. For example, the four different carbon centers of $F_3CC(O)OC_2H_5$

exhibit a total spread of $\Delta(\mathrm{IE}_{\mathrm{C\,1s}}) = 8$ eV. This is quite large. However, relative to $\mathrm{IE}_{\mathrm{C\,1s}} \simeq 290$ eV, it amounts to only 3%. Thus, a perturbation theory approach seems appropriate.

Core orbitals can be supposed to be highly localized on their respective centers (i.e., to be highly contracted atomic orbitals). As a result of this strong nuclear coupling, all the other atomic centers and valence electrons can be thought of as being relatively "far away". These suppositions suggest that electron–electron interactions can be treated in a simple Coulombic fashion.

a. Point-Charge Potential Model

We start by applying Koopmans' theorem to a core orbital $\varphi_{\mathrm{A}}^{\mathrm{c}}$ of atom A

$$\begin{aligned}\mathrm{IE}_{\mathrm{c}}^{\mathrm{A}} &= -\epsilon_{\mathrm{A}}^{\mathrm{c}} \\ &= -\langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)|\mathcal{T}(1)|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\rangle - \langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)|Z_{\mathrm{A}}/r_{\mathrm{A}1}|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\rangle \\ &\quad - \sum_{\mathrm{c}'\text{ on A}} \langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi_{\mathrm{A}}^{\mathrm{c}'}(2)|[(1-\mathcal{P}_{12})/r_{12}]|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi_{\mathrm{A}}^{\mathrm{c}'}(2)\rangle \\ &\quad + \sum_{\mathrm{B}\neq\mathrm{A}} \{\langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)|Z_{\mathrm{B}}/r_{\mathrm{B}1}|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\rangle \\ &\quad - \sum_{k\text{ on B}} \langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi_{\mathrm{B},k}^{\mathrm{c}}(2)|[(1-\mathcal{P}_{12})/r_{12}]|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi_{\mathrm{B},k}^{\mathrm{c}}(2)\rangle\} \\ &\quad - \sum_{\mathrm{v}} \langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi^{\mathrm{v}}(2)|[(1-\mathcal{P}_{12})/r_{12}]|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi^{\mathrm{v}}(2)\rangle \qquad (96)\end{aligned}$$

The various terms of eq 96, in succession, represent kinetic energy; attraction by the nucleus A; interaction with core electrons on A; interaction with nuclei and core electrons of atoms B $\neq$ A; and, finally, interaction with the valence electron system. Since the last three terms are the only ones which involve atomic centers B $\neq$ A and the valence electron system, only these will change upon going from one molecule to another.

We now introduce the following approximations.[44]

In line with standard practice in perturbation theory, we will use $\varphi_{\mathrm{A}}^{\mathrm{c}}$, unchanged, for the core orbital of atom A, regardless of the molecule of which atom A is a constituent.

The valence orbitals are given by the LCAO expression

$$\varphi_k^{\mathrm{v}} = \sum_l \chi_l c_{lk} \qquad (97)$$

The ZDO (i.e., zero differential overlap) approximation in the form

$$\langle\chi_l(1)\chi_m(2)|1/r_{12}|\chi_n(1)\chi_o(2)\rangle = \delta_{ln}\delta_{mo}\gamma_{lm} \qquad (98)$$

is used consistently.

All two-center terms are replaced by the classical expressions

$$\langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)|Z_{\mathrm{B}}/r_{\mathrm{B}1}|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\rangle = Z_{\mathrm{B}}/R_{\mathrm{AB}} \qquad (99)$$

$$\langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi_{\mathrm{B},k}^{\mathrm{c}}(2)|1/r_{12}|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\varphi_{\mathrm{B},k}^{\mathrm{c}}(2)\rangle = 1/R_{\mathrm{AB}} \qquad (100)$$

$$\langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\chi_{\mathrm{B},l}(2)|1/r_{12}|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\chi_{\mathrm{B},l}(2)\rangle = 1/R_{\mathrm{AB}} \qquad (101)$$

All one-center core/valence interaction integrals are replaced by an average value

$$\langle\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\chi_{\mathrm{A},m}(2)|1/r_{12}|\varphi_{\mathrm{A}}^{\mathrm{c}}(1)\chi_{\mathrm{A},m}(2)\rangle = \gamma_{\mathrm{vc}}^{\mathrm{A}} \qquad (102)$$

The valence charge of atom X, which possesses N_{X} core electrons, is given by

$$q_{\mathrm{X}} = Z_{\mathrm{X}} - N_{\mathrm{X}} - \sum_{\mathrm{v}\in\mathrm{occ}} \sum_{l\text{ on X}} c_{l\mathrm{v}}^2 \qquad (103)$$

If the change in the valence charge caused by placing atom X into a molecule is represented by

$$\Delta q_{\mathrm{X}} = q_{\mathrm{X}} - q_{\mathrm{X}}^0 \qquad (104)$$

where q_{X}^0 refers to a free atom X, it follows from eq 97–104 that the change in core-ionization energy is given by

$$\Delta(\mathrm{IE}_{\mathrm{c}}^{\mathrm{A}}) = -\Delta q_{\mathrm{A}}\gamma_{\mathrm{vc}}^{\mathrm{A}} - \sum_{\mathrm{X}\neq\mathrm{A}} \Delta q_{\mathrm{X}}/R_{\mathrm{AX}} \qquad (105)$$

The physical interpretation of eq 105 is simple. It takes more energy to remove an electron from a core orbital of A when A is positively charged, and less energy when all atoms X $\neq$ A are negatively charged. Several equations similar to eq 105 have been used successfully to correlate chemical shift data. Of these, we list only

$$\Delta(\mathrm{IE}_{\mathrm{c}}^{\mathrm{A}}) = aq_{\mathrm{A}} + b \qquad (106)$$

and

$$\Delta(\mathrm{IE}_{\mathrm{c}}^{\mathrm{A}}) = cq_{\mathrm{A}} + \sum_{\mathrm{X}\neq\mathrm{A}} q_{\mathrm{X}}/R_{\mathrm{AX}} + d \qquad (107)$$

Both of these equations exhibit considerable similarities to eq 105.

b. Critique of the Point Charge Potential Model

The point charge model has been exceedingly successful. Despite this, it suffers some drawbacks:

Equation 105 may be used in conjunction with quantum chemistry to calculate values of $\Delta(\mathrm{IE}_{\mathrm{c}}^{\mathrm{A}})$. The quantity to be calculated is the atomic valence charge q_{X} of *every* atomic center in the molecule. The calculation of q_{X} for center X devolves on the calculation of the valence electron population, P_{X}, on center X, and it is at this point that ambiguity enters.[45] The electron population of an atom in a molecule is not a precisely defined quantity. A precise definition would require a partitioning of the whole molecular space into atomic subspaces, and a means of allocating the electronic charge which is located at the boundaries between these subspaces to the contiguous subspaces. Unfortunately, there is no "correct" way of doing this. Hence, the relation of eq 105 to quantum chemistry is operationally ill-defined.

The second term of eq 105 is not small relative to the magnitudes of chemical shifts. Hence, it cannot be neglected.

The removal of a core electron is equivalent to replacing the original nucleus of atomic number Z_{A} by one of atomic number $Z_{\mathrm{A}} + 1$. This viewpoint constitutes the basic idea of the "Equivalent Core" approach.[46] To the extent that this view be correct, it follows that some degree of orbital contraction must occur during or after the core ionization event. If the orbital relaxation is a fast process and if it can proceed to any significant degree during the time required for ionization, it can and will introduce changes in $\Delta(\mathrm{IE}_{\mathrm{c}}^{\mathrm{A}})$. These, of course, will affect eq 105.

c. Modification of Koopmans' Theorem for Inner Shells

The orbital picture is well suited to a discussion of valence ionizations and is moderately good for valence → Rydberg excitations. With some reservations, it is also useful for core ionizations and even intravalence excitations. However, the orbital description can be carried one step further; in fact, it can be modified to take account of all "shake-up" and "shake-off" satellite events. We will now investigate this modification. We will enquire into the nature of the experimental quantity to which an orbital energy can be related when some of the approximations inherent in Koopmans' theorem are physically unrealistic.

We start with an eigenfunction Ψ^N of the N-electron system[47]

$$\mathcal{H}_{\mathrm{el}}^N\Psi^N = E_{\mathrm{el}}^N\Psi^N \qquad (108)$$

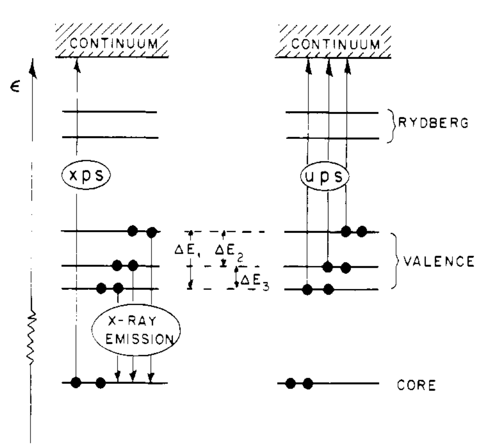


Figure 12. The relationship of x-ray emission energies to UPS ionization energies.

where $\Psi^N = \psi_0^N$ is a single Slater determinant. As previously, we generate the configuration wave function ψ_{-k}^{N-1} by removing the electron which is in the orbital φ_k of ψ_0^N. The wave function ψ_{-k}^{N-1} is not an eigenfunction of the cationic Hamiltonian, $\mathcal{H}_{\mathrm{el}}^{N-1}$. However, it can be expanded in terms of the complete set[48] of eigenfunctions, $\{\Psi_l^{N-1}\}$, of $\mathcal{H}_{\mathrm{el}}^{N-1}$. Thus, we find

$$\psi_{-k}^{N-1} = \sum_l \Psi_l^{N-1} c_{lk} \tag{109}$$

where

$$\mathcal{H}_{\mathrm{el}}^{N-1} \Psi_l^{N-1} = E_{\mathrm{el},l}^{N-1} \Psi_l^{N-1} \tag{110}$$

The probability of finding the cationic system in one of its eigenstates Ψ^{N-1} when an electron is ionized out of the orbital φ_k of the parent N-electron system is[49]

$$P_{k\rightarrow l} \propto c_{lk}^2 \tag{111}$$

Therefore, the orbital energy ϵ_k is

$$-\epsilon_k = \sum_l \mathrm{IE}_l c_{lk}^2 \Big/ \sum_l c_{lk}^2 \tag{112}$$

which, in turn, is simply the weighted ionization energy

$$-\epsilon_k = \sum_l \mathrm{IE}_l I_l \Big/ \sum_l I_l \tag{113}$$

where I_l is the intensity of the ionization process IE_l, and the summation runs over all cationic states which can be achieved by removal of an electron from the orbital φ_k of ψ_0^N (i.e., over the main ionization event and all satellite "shake-up" and "shake-off" events).[50]

It is in this way that one retains the idea of ionization as a removal of an electron from one specific orbital. Although the processing of eq 113 might seem difficult, it turns out that it is quite simple in an experimental sense: The identification of the "main line"/"shake-up"/"shake-off" events is not too difficult even when orbital relaxation effects are large.

2. Core Excitations

The core excitations of an N-electron system are of two kinds: core → valence and core → Rydberg. The energies of these absorption events usually fall in the x-ray region. Subsequent to a core ionization event, the heavily excited ($N-1$)-electron system may decay by filling the core vacancy, emitting either an additional electron (i.e., Auger effect) or a photon (i.e., x-ray emission).

The intensities of an x-ray absorption or emission event can be used to obtain information on the LCAO coefficients of a valence orbital ϕ_{v}, or, by means of the "equivalent core approximation", one can obtain information on molecular radicals which cannot be ascertained by any other means. We will discuss each of these in turn.

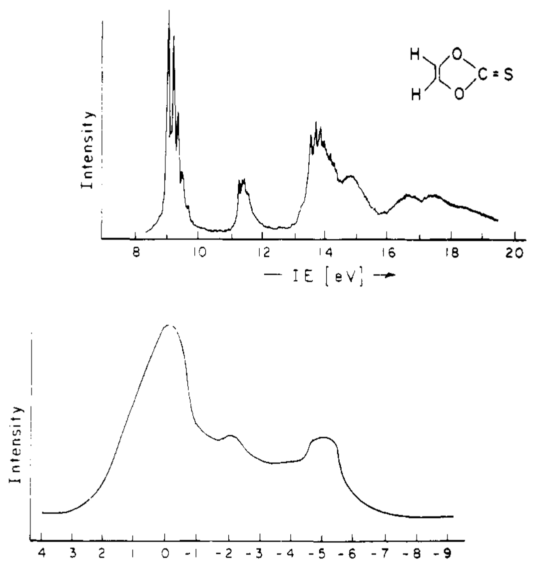


Figure 13. Photoelectron (top) and x-ray emission (bottom) spectra for vinylene thionocarbonate. The energy scale on the bottom spectrum is relative only. Intensity scales are linear.

a. Shapes of Valence Orbitals[51]

The x-ray emission of the core-ionized cation can be discussed as a transition from a core vacancy to a valence vacancy

$$\psi_{-\mathrm{c}}^{N-1} \rightarrow \psi_{-\mathrm{v}}^{N-1} \tag{114}$$

The intensity of such a transition, as given by the electric-dipole approximation, is

$$\begin{aligned} I_{\mathrm{cv}} &\propto (\Delta E)^3 \left| \left\langle \psi_{-\mathrm{c}}^{N-1} \right| \sum_{i=1}^{N-1} \mathbf{r}_i \left| \psi_{-\mathrm{v}}^{N-1} \right\rangle \right|^2 \\ &\propto (\Delta E)^3 \left| \langle \phi_{\mathrm{v}}(1) | \mathbf{r}_1 | \phi_{\mathrm{c}}(1) \rangle \right|^2 \end{aligned} \tag{115}$$

The two-center terms of eq 115 can be neglected with a fair degree of assurance, whereupon it reduces to a sum of one-center, atomic, transition moments for which, individually, the atomic g ↔ u selection rules are valid. Thus, if we neglect the energy-dependent term, the x-ray emission intensities for a $\phi_{\mathrm{v}} \rightarrow \phi_{1\mathrm{s}}$ transition are proportional to the sum of the squares of the coefficients of the p AO's in the LCAO expansion of ϕ_{v}. That is

$$I_{\mathrm{cv}} \propto \sum_{k \text{ on A}} c_{k\mathrm{v}}^2 \left| \langle \phi_{\mathrm{c}}^{\mathrm{A}} | \mathbf{r} | \chi_k \rangle \right|^2 \propto \sum_{\substack{k \text{ on A} \\ k \in \mathrm{p}}} c_{k\mathrm{v}}^2 \tag{116}$$

where, according to Koopmans' theorem, the orbitals $\phi_{\mathrm{c}}^{\mathrm{A}}$ and χ_k are those pertinent to the N-electron system.

The process of a core ionization which is followed by x-ray emission of valence → core type, is shown on the left of Figure 12. The final states achieved after the x-ray emission are Koopmans' configurations of type $\psi_{-\mathrm{v}}^{N-1}$. The process of valence ionization is shown on the right of Figure 12. The final states achieved are, again, Koopmans' configurations $\psi_{-\mathrm{v}}^{N-1}$. Hence, as should be obvious from Figure 12, the energy differences ΔE_1, ΔE_2, and ΔE_3 between the different x-ray emission lines should be equal to those of the corresponding UPS bands. These equalities between UPS data for the N-electron system and x-ray emission data for the $N-1$ electron system, particularly when coupled with the stringent g/u atomic selection rule properties, provide a very powerful means of assigning UPS bands.[51-53]

An example is provided by vinylene thionocarbonate. The photoelectron spectrum of this molecule is shown in Figure 13.

The first structure in the photoelectron spectrum between 8 and 10 eV may represent one or two ionization events, relating to either the first π orbital, π_1, or the sulfur lone pair orbital, n_S, or both of these. A decision between these three possibilities can be made on the basis of the sulfur Kβ spectrum: Appreciable Kβ intensity will appear only if the valence orbital (in which the final hole occurs) has a high contribution of sulfur 3p orbitals. The n_S and the π_1 valence orbitals satisfy this condition. The fact that there is only one strong peak in the x-ray emission spectrum suggests, therefore, that the photoelectron structure between 8 and 10 eV corresponds to two ionization events. Placing either the π_1 or the n_S ionization event near 11 eV (the second peak in the photoelectron spectrum) and the other near 9 eV would be expected to produce a very different type of x-ray spectrum. This conclusion has been verified by extended Hückel MO calculations[53] in conjunction with eq 116.

A similar argument applies to the x-ray absorption spectroscopy of the *N*-electron system. Thus, a study of $1s_A \rightarrow$ Rydberg transitions should provide some insight into the shape of Rydberg orbitals.

b. Equivalent-Core Approach[54]

The discussion of section a above assumes a complete absence of relaxation effects. By way of contrast, it is electronic relaxation effects which provide the central motif of the equivalent-core approximation.

Since the radius of an inner shell is small relative to the valence shell, it is thought that a 1s hole on center A is fully equivalent to an increase of the atomic number of center A by one unit. The 1s hole is filled by adding an extra electron while, at the same time, the atomic number is increased from Z to $Z + 1$ by adding an extra proton to the nucleus. Thus, the terminal orbitals of a 1s → nR excitation of CH_4 should be the same as those of an NH_4 molecule. The relationships between the various states of CH_4 and NH_4, both Rydberg excited and core ionized, are shown in Figure 14. These relationships are self-evident. The more replete use of the equivalent core approach, as practiced by Schwarz[54] to obtain information for radicals such as $NH_4\cdot$ and $PH_4\cdot$, is shown in Figure 15.

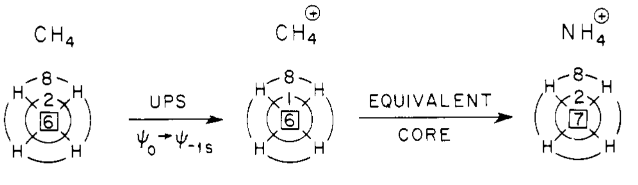
3. *Significance of Relaxation*

The viewpoints presented in sections 2.a and 2.b treat electronic relaxation from two diagonally opposed points of view. In order to obtain approximate information for the shapes of valence orbitals, as in 2.b, we either neglect electronic relaxation effects or presume them to be small. The equivalent core approach of 2.b, on the other hand, presumes the electronic relaxation effects to be so large as to vindicate the replacement of atom C (which contains a core vacancy) by atom N (which contains no core vacancy).

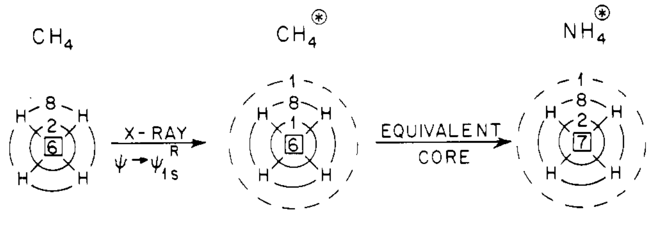
In addition to electronic relaxation effects, one must also be wary about the possibility of the relaxation of molecular geometry. This bears on the attitudes of sections 2.a and 2.b.

(i) The core vacancy → valence vacancy transition observed in x-ray emission spectroscopy occurs near or at the equilibrium geometry of the core ionized species, say CH_4^+ (C $1s^{-1}$). Differences in the vertical transition energies (Figure 12), therefore, are slightly different from those observed in photoelectron spectroscopy, where the vertical transition energies refer to the equilibrium geometry of the neutral species. By the equivalent core approach, the geometry of CH_4^+ (C $1s^{-1}$) should be close to the geometry of NH_4^+, which certainly is quite different from that of CH_4.

(ii) Differences between x-ray absorption peaks, say those of SiH_4, are considered to be equal to the energy differences associated with excitations of the $Z + 1$ species, PH_4. However, it is clear that this statement is correct only insofar as one gets information on the energy levels of $PH_4^{\cdot}$ at the geometry of SiH_4 (neutral), which again is quite different from the $PH_4\cdot$ equilibrium geometry.



A CORE IONIZATION EVENT



A RYDBERG EXCITATION

Figure 14. A diagram of a core ionization and a core → Rydberg excitation from the point of view of the equivalent core assumption. The atomic number, 6 or 7, is enclosed in a square, the C 1s or N 1s shell is denoted by the circle immediately adjacent to the square. The valence shell is denoted by the outermost solid circle. The Rydberg orbital is denoted by the dashed circle.

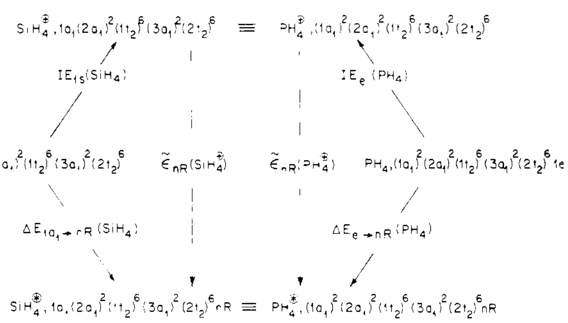


Figure 15. The relationship between various states of SiH_4 and PH_4 as obtained using the equivalent-core approximation. It is clear that one may use data for SiH_4 to obtain information for a molecular radical PH_4.

These questions of relaxation, both electronic and geometric, would completely invalidate the attitudes of section 2, if carried to their extremes. Fortunately, the resolution attendant to x-ray studies has been quite limited, and these sorts of difficulties have not yet arisen. Resolution, however, is improving, and the future will certainly show significant discrepancies from the simple picture presented in section II.A.2.

D. Orbital Perspective

We hope the reader will agree that we have been reasonably successful in describing a great variety of spectroscopic results within the confines of the MO concept. Indeed, it was clear from the outset that success would be ours: That, after all, is what we set out to achieve! Anyway, it seems clear that the MO concepts would not be so popular, if they were not also useful, and it is not surprising that we should concur in this conclusion.

We hope, however, that our success has been of a slightly different turn. It was not ab initio obvious, we think, that we could provide a theoretical justification for the MO approach in all, or even many of the instances in which we have used it. The fact that we have been able to provide such justifications, regardless of how heuristic they might be, encourages us to delve further into the basis for MO success, past and future. This, we now proceed to do.

The basic desideratum in any discussion of electronic transitions is to reduce the problem from one which involves two different states, each described by a (multi)determinantal wave function, to one which involves one single set of orbitals. The ability to reduce the problem in such a way hinges on the twin difficulties of electron correlation and relaxation effects. The change of correlation energy between the two states must be small, and the relaxation effects must not be so large that they inhibit a one-to-one correspondence of the orbitals of one electronic state with those of the other.

The use of terms such as "an electron is excited from one orbital to another" implies that the orbitals do not change much during the course of a transition. To the extent that such a statement is valid, it is implied that the orbitals in the two states are either identical or so similar that a knowledge of them in one state is adequate for the identification of them in another. In the same way, a great deal of experience indicates that the similarities between certain electronic states of quite different molecular entities can be translated into a requirement for similarity at the orbital level. Thus, very simple (i.e., one-electron) perturbation schemes can be used to describe the electronic states of one molecule in terms of those of another related molecule.

We now synopsize some of the more pertinent theoretical characteristics of the MO approach. We do so in terms of one-, two-, and many-orbital properties.

One-Orbital Properties.[55] These consist of ionization energies and electron affinities. Both of these events can be described in terms of one single orbital energy. The theoretical justification for such a description is vested in Koopmans' theorem. The second part of Koopmans' theorem states that the canonical MO's of the N-electron system are also optimal (i.e., "good") for the $(N - 1)$-electron system. The experimental evidences, based on the near identity of IE_n with $-\epsilon_n$ and on the general correctness of the selection rule for photoelectron spectroscopy, constitute the best "proof" of the orbital structure of both atoms and molecules. Not surprisingly, this "goodness" holds not only for the familiar valence orbitals, but also for the strongly coupled core orbitals.

Two-Orbital Properties. These, for the most part, consist of electronic transitions. At best, these cannot be described by less than two orbitals. However, there exists no one set of optimal orbitals which is adequately descriptive of different excited states; configuration interaction must be considered from the outset. In addition to the nonexistence of a single set of orbitals which is "good" for a large number of different states, difficulties arise in connection with the degeneracies due to spatial and spin (i.e., permutational) symmetry. As a result of this unfortunate situation, computational and interpretational problems are rather severe in VIS, UV, and VUV spectroscopy. And, as a further consequence, the number of excited state assignments which meet with general accord are relatively few. In view of all these difficulties, we suggest that electronic spectra are best discussed within the "optimum excited state orbital" framework. These OES orbitals should be extremely useful for limited classes of transitions (i.e., all those which arise by excitation from one fixed orbital).

Many-Orbital Properties. These may include one-electron properties such as dipole moments or electron densities. They also include total energies. There is no specific reason to prefer any particular set of orbitals (e.g., canonical) in these instances. However, since it really does not matter[14] which kind of orbitals one uses, the canonical set is just as good as any other Hartree–Fock set. Although there is little or no theoretical reason to expect that a *simple* description of many-orbital properties should obtain, chemical ingenuity, by subsuming different physicochemical effects into one or a few parameters, has achieved a considerable simplicity even in these difficult areas.

We conclude, therefore, that canonical MO's are most appropriate for one-orbital properties, that OES MO's may well be those of choice for two-orbital properties, and that any set of HF MO's is just as good as any other for many-orbital properties. We also conclude that the basic MO idea (i.e., the use of a single determinant to describe a many-electron wave function) is surprisingly excellent.

III. Orbital Interaction

We have been concerned, so far, with the MO description of electronic excitation and ionization events. We have emphasized those aspects for which the molecular orbital structure of the parent, ground-state, N-electron system could be used to advantage. We have established the approximations involved in this approach and have outlined its merits and demerits. Having come so far, we now wish to discuss the concept of chemical relatedness on an "exact" MO level. Our aim is to fit the many popular, and often very qualitative, ideas about molecular relatedness into a properly constructed theoretical niche.

A. General Formalism for Orbital Interactions

We will decompose a molecule AB into two bits, A and B, and we will try to use the information which is available for these bits in order to construct a description of the composite system, AB. It is obvious that such an attempt should lead, if successful, to some kind of perturbation approach.

Let $\mathcal{F}$ be the Fock operator for AB, and $\mathcal{F}^{\mathrm{A}}$ and $\mathcal{F}^{\mathrm{B}}$ be those for the bits A and B, respectively. Then

$$\mathcal{F} = \mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}} \qquad (117)$$

where

$$\mathcal{F}^{\mathrm{AB}} = \mathcal{F} - \mathcal{F}^{\mathrm{A}} - \mathcal{F}^{\mathrm{B}} \qquad (118)$$

and where the sets $\{\phi_i^{\mathrm{A}}\}$, $\{\phi_i^{\mathrm{B}}\}$ and $\{\phi_i^{\mathrm{AB}}\}$ are eigenfunctions of the Fock operators.

$$\mathcal{F}^{\mathrm{A}}\phi_i^{\mathrm{A}} = \epsilon_i^{\mathrm{A}}\phi_i^{\mathrm{A}} \qquad (119)$$

$$\mathcal{F}^{\mathrm{B}}\phi_i^{\mathrm{B}} = \epsilon_i^{\mathrm{B}}\phi_i^{\mathrm{B}} \qquad (120)$$

$$\mathcal{F}^{\mathrm{AB}}\phi_i^{\mathrm{AB}} = \epsilon_i^{\mathrm{AB}}\phi_i^{\mathrm{AB}} \qquad (121)$$

We seek an expansion of the MO's ϕ^{AB} in terms of the MO sets $\{\phi_i^{\mathrm{A}}\}$ and $\{\phi_i^{\mathrm{B}}\}$. Such an expansion can be made exactly: Since the sets $\{\phi_i^{\mathrm{A}}\}$ and $\{\phi_i^{\mathrm{B}}\}$ are complete, the set $\{\phi_i^{\mathrm{A}}\} \otimes \{\phi_i^{\mathrm{B}}\} = \{(\phi_i^{\mathrm{A}}, \phi_j^{\mathrm{B}})\}$ is also complete. Prior to obtaining an exact solution for the ϕ_i^{AB}, and in order to retain as much chemical pertinence as possible, we subdivide each of $\{\phi_i^{\mathrm{A}}\}$ and $\{\phi_i^{\mathrm{B}}\}$ into two subsets, one for occupied and one for unoccupied orbitals. The terms "occupied" and "unoccupied", in turn, are defined relative to the ground configurations of the two bits A and B.

The secular determinant, $|\boldsymbol{F} - \boldsymbol{ES}| = 0$, is given in eq 122 and is blocked according to the set subdivisions $\{\phi_{\mathrm{unocc},i}^{\mathrm{A}}\}$, $\{\phi_{\mathrm{occ},i}^{\mathrm{A}}\}$, $\{\phi_{\mathrm{unocc},i}^{\mathrm{B}}\}$, and $\{\phi_{\mathrm{occ},i}^{\mathrm{B}}\}$. This determinant (eq 122)

$$\begin{array}{ccccc} & \{\phi_{\mathrm{unocc},i}^{\mathrm{A}}\} & \{\phi_{\mathrm{occ},i}^{\mathrm{A}}\} & \{\phi_{\mathrm{occ},i}^{\mathrm{B}}\} & \{\phi_{\mathrm{unocc},i}^{\mathrm{B}}\} \\ \{\phi_{\mathrm{unocc},i}^{\mathrm{A}}\} & \mathrm{I} & \mathrm{VI} & \mathrm{VII} & \mathrm{VIII} \\ \{\phi_{\mathrm{occ},i}^{\mathrm{A}}\} & \mathrm{VI}^{\mathrm{T}} & \mathrm{II} & \mathrm{V} & \mathrm{VIIa} \\ \{\phi_{\mathrm{occ},i}^{\mathrm{B}}\} & \mathrm{VII}^{\mathrm{T}} & \mathrm{V}^{\mathrm{T}} & \mathrm{III} & \mathrm{VIa} \\ \{\phi_{\mathrm{unocc},i}^{\mathrm{B}}\} & \mathrm{VIII}^{\mathrm{T}} & \mathrm{VIIa}^{\mathrm{T}} & \mathrm{VIa}^{\mathrm{T}} & \mathrm{IV} \end{array} = 0 \qquad (122)$$

is symmetric in the principal diagonal.

The matrix elements which enter various blocks are typified in the following.

Block I (or IV, by the interchange A ↔ B): A typical matrix element is

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{unocc},j}\rangle - E\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\phi^{\mathrm{A}}_{\mathrm{unocc},j}\rangle \\ = (\epsilon^{\mathrm{A}}_i - E\delta_{ij}) + \langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{unocc},j}\rangle \end{aligned} \quad (123)$$

Block II (or III, by the interchange A ↔ B): A typical matrix element is

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle - E\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle \\ = (\epsilon^{\mathrm{A}}_i - E\delta_{ij}) + \langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle \end{aligned} \quad (124)$$

Block V: A typical matrix element is

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle - E\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle \\ = (\epsilon^{\mathrm{A}}_i + \epsilon^{\mathrm{B}}_j - E)\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle + \langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle \end{aligned} \quad (125)$$

Block VI (or VIa, by the interchange A ↔ B): A typical matrix element is

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle - E\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle \\ = \langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle \end{aligned} \quad (126)$$

Block VII (or VIIa, by the interchange A ↔ B): A typical matrix element is

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle - E\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle \\ = (\epsilon^{\mathrm{A}}_i + \epsilon^{\mathrm{B}}_j - E)\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle \\ + \langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{occ},j}\rangle \end{aligned} \quad (127)$$

Block VIII: A typical matrix element is

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{unocc},j}\rangle - E\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\phi^{\mathrm{B}}_{\mathrm{unocc},j}\rangle \\ = (\epsilon^{\mathrm{A}}_i + \epsilon^{\mathrm{B}}_j - E)\langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\phi^{\mathrm{B}}_{\mathrm{unocc},j}\rangle \\ + \langle \phi^{\mathrm{A}}_{\mathrm{unocc},i}|\mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{B}}_{\mathrm{unocc},j}\rangle \end{aligned} \quad (128)$$

In the simplification leading to eq 125, 127, and 128, we use the hermitian property of the $\mathcal{F}$'s, namely

$$\langle \phi^{\mathrm{A}}_i|\mathcal{F}^{\mathrm{A}}|\phi^{\mathrm{B}}_j\rangle = \langle \mathcal{F}^{\mathrm{A}}\phi^{\mathrm{A}}_i|\phi^{\mathrm{B}}_j\rangle = \epsilon^{\mathrm{A}}_i\langle \phi^{\mathrm{A}}_i|\phi^{\mathrm{B}}_j\rangle \quad (129)$$

It will be noted that the matrix elements in blocks V and VIII are identical with the Mulliken–Wolfsberg–Helmholtz expression

$$F_{ij} = K[\epsilon_i + \epsilon_j)/2]S_{ij} \quad (130)$$

when $K = 2$ and when $\mathcal{F}^{\mathrm{AB}}$ is zero. The operator $\mathcal{F}^{\mathrm{AB}}$ will be small if the electron density of the composite system is merely a simple superposition of those of the bits A and B, (i.e., when $\psi^{\mathrm{AB}} = \mathcal{A}\psi^{\mathrm{A}}\psi^{\mathrm{B}}$). Consequently, eq 130 is expected to hold best for nonpolar, weakly interacting systems. The operator $\mathcal{F}^{\mathrm{AB}}$ consists, minimally, of the kinetic energy operator which is contained in both $\mathcal{F}^{\mathrm{A}}$ and in $\mathcal{F}^{\mathrm{B}}$ and which does not drop out upon forming $\mathcal{F}^{\mathrm{AB}}$ (eq 118). This identity provides a starting point for more elaborate equations for the off-diagonal elements.[56]

B. Hierarchy of Approximations

No approximations, beyond the MO approximation for A, B, and AB, have been made so far. Even the electron density in AB can be considered to be self-consistent because $\mathcal{F}^{\mathrm{AB}} = \mathcal{F} - \mathcal{F}^{\mathrm{A}} - \mathcal{F}^{\mathrm{B}}$ refers to the final, best Fock operator. However, since it is our stated purpose to provide a good foundation for certain primitive MO concepts, we now investigate the approximations which must be introduced into the exact eq 122 in order to generate these primitive concepts. The general idea is to reduce the size of the secular determinant considerably, even to a 2 × 2, if this be feasible (this, of course, is the gist of the frontier orbital theory, as developed by Fukui[57]); and to neglect as many matrix elements as possible. The guidelines in any instance will be determined by the concept one wishes to extract. In general, one will extract the concept from eq 122 by retaining the minimum size of the determinant and neglecting the maximum number of elements. The eigenvalues may then be obtained either by matrix diagonalization or by perturbation theory.

This procedure is the essence of all orbital interaction concepts. We now discuss several such concepts. We begin with the most drastic set of approximations.

1. Ground-State Properties

The ground state of AB can be related to those of A and B only if blocks VI, VII, VIa, and VIIa are small. In essence, this requirement implies that only small changes of the electron density distribution occur during the conjunction A + B → AB. As a result, we will divide this section into two types of interactions: those that allow little or no change of electron distribution during the conjunction and those that permit a larger change.

a. Interactions of the Occupied MO Subsets

If the overlap of the subsets $\{\phi^{\mathrm{A}}_{\mathrm{occ},i}\}$ and $\{\phi^{\mathrm{B}}_{\mathrm{occ},i}\}$ is zero, the interactions of these two subsets will produce no change in the electron density distribution. In other words, the electron density distribution in AB will be a simple superposition of that for A and that for B. Thus, in the limit $S = 0$, these interactions are those for which the ground-state charge density distribution is an invariant.

By construction, we set blocks VI, VII, VIa, and VIIa equal to **O**. The individual MO's $\phi^{\mathrm{AB}}_{\mathrm{occ},i}$ may then be formed from the sets $\{\phi^{\mathrm{A}}_{\mathrm{occ},i}\}$ and $\{\phi^{\mathrm{B}}_{\mathrm{occ},i}\}$. In fact, we write

$$\psi^{\mathrm{AB}} = \mathcal{A}_{\mathrm{AB}}(\psi^{\mathrm{A}}\psi^{\mathrm{B}}) \quad (131)$$

where $\mathcal{A}_{\mathrm{AB}}$, the residual antisymmetrizing operator, merely permutes the electrons in ψ^{A} with those in ψ^{B}. The only remaining parts of the secular determinant of eq 122 are

$$\begin{vmatrix} \mathrm{II} & \mathrm{V} \\ \mathrm{V} & \mathrm{III} \end{vmatrix} = 0 \quad (132)$$

Consequently, the transformation to the canonical orbital set $\{\phi^{\mathrm{AB}}_{\mathrm{occ},i}\}$ is induced by the matrix elements of block V.

This particular set of suppositions is known as the linear combination of bond orbitals (LCBO).

The diagonal elements may be written

$$\begin{aligned}\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},i}\rangle \\ = \epsilon^{\mathrm{A}}_i + \langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},i}\rangle \quad (133) \\ \simeq \epsilon^{\mathrm{A}}_i \quad (134)\end{aligned}$$

The off-diagonal elements (e.g., those of block II) are given by eq 124 as

$$\langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{A}} + \mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle = \langle \phi^{\mathrm{A}}_{\mathrm{occ},i}|\mathcal{F}^{\mathrm{B}} + \mathcal{F}^{\mathrm{AB}}|\phi^{\mathrm{A}}_{\mathrm{occ},j}\rangle \quad (135)$$

$$\simeq 0 \quad (136)$$

The use of eq 134 and 135 implies a neglect of all inductive effects.[58] The particular set which may be used (i.e., whether eq 133 and 135, 133 and 136, etc.) is a matter of either taste or expediency.

Finally, we presume that the major interactions can be confined to a few orbitals of subsets $\{\phi^{\mathrm{A}}_{\mathrm{occ},i}\}$ and $\{\phi^{\mathrm{B}}_{\mathrm{occ},i}\}$. This supposition leads to the listing of the orbital interaction concepts given in Table IX. The size of Table IX indicates that these concepts are quite plentiful. It is also obvious that some of them possess very graphic names. Nonetheless, all of them, regardless of how superficially different they might appear, derive from eq 122 via the same set of approximations; they differ only in the orbital types which interact and all of them may or may not include inductive components.

Numerous examples are contained in the literature.[2,17] Therefore, we restrict ourselves here to the case of norbornadiene.[66] Norbornane does not exhibit any sharp photoelectron bands, whereas norbornene displays one well-defined peak at

TABLE IX. Various Types of Orbital Interaction Concepts[59]

Name	A, B, . . .	$\phi^A_{occ}, \phi^B_{occ}$	AB . . .	ϕ^{AB} . . .	Ref
π conjugation	A B } ethylene	ϕ^A ϕ^B } π orbital on ethylene	Butadiene	π orbitals in butadiene	60
	A, benzene B, ammonia	ϕ^A, π orbitals on benzene ϕ^B, lone-pair orbital on ammonia	Aniline	π orbitals in aniline	61
Hyperconjugation	A, benzene B, methane	ϕ^A, π orbitals on benzene ϕ^B, π-type orbital in methane	Toluene	π orbitals in toluene	2c
Through-space[a] interaction	A B } ethylene	ϕ^A ϕ^B } π orbitals	Norbornadiene	π-type orbitals	62
Bond–bond interaction	A B } disilane	ϕ^A ϕ^B } Si–Si bond orbitals	Trisilane	Si–Si bond orbitals	63
Through-bond[a] interaction	A_1 A_2 } trimethyl-amine	ϕ^{A_1} ϕ^{A_2} } lone-pair orbitals	1,4-Diazabicyclo-[2.2.2]octane	Lone-pair orbitals in Dabco	64

[a] "Through-space" and "through-bond" interactions can be separated by first allowing for "through-space" effects among equivalent orbitals and then discussing the interactions (i.e., "through-bond") between equivalent orbitals.[65]

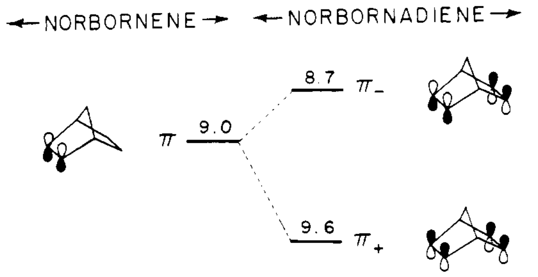


Figure 16. "Through-bond" interaction in norbornadiene. The numbers indicate the corresponding ionization potentials (in eV).

9.0 eV, which is assigned as $I(\pi)$. The value of $I(\pi)$ for ethylene[2a] is 10.5 eV, the 1.5-eV shift to norbornene being in line with alkylation and ring-closure effects. The introduction of a second double bond yields norbornadiene, which exhibits two well-defined bands at 8.7 and 9.6 eV. The 0.9-eV splitting is usually attributed to "through-space" interactions.[65,66] The norbornane–norbornadiene situation is diagrammed in Figure 16. This demonstrates several important points: (a) the attitude works, but it works best for selected orbitals, namely those which are either highly atomic (localized or lone pair) or well-separated from all others; (b) the choice of the bits A and B is not well defined (if one chose ethylene as the basic unit, the diagram of Figure 16 would look much less convincing); (c) the splitting is not symmetrical (consequently, the full problem of eq 122 is only approximately reducible to a 2 by 2 matrix).

b. Interactions of Occupied and Unoccupied MO's

The primary interactions, in this instance, occur between $\{\phi^M_{occ,i}\}$ with $\{\phi^M_{unocc,i}\}$, where $M \in \{A,B\}$. Such interactions, even when the overlaps $\langle \phi^A_{occ,i} | \phi^B_{occ,j} \rangle = 0$, lead to a change of the electron density distribution in AB. In other words, even in the limit of no overlap, the electron density distribution in AB is not a simple superposition of that of A and that of B.

Two extreme cases arise within the orbital interaction classification scheme. These are the following.

Polarization.[53,67] The polarization of the electron distribution within subsystem A (or B) is achieved by considering the matrix elements of block VI (or VIa). The primary effect is a mixing of the unoccupied orbitals on one bit with occupied orbitals on the same bit.

Charge Transfer.[68] Charge transfer from A to B (or vice versa) is achieved by inclusion of the matrix elements of block VII (or VIIa). The primary effect is a mixing of the unoccupied orbitals of one bit with occupied orbitals of the other bit.

2. Excited-State Properties

The number of excited states which are possible in a molecule AB is very much larger than the sum of those for the bits A and B separately. As a result, the ability to enumerate and/or classify such states on an MO interaction model would be of considerable value. Unfortunately, this does not appear to be entirely possible.

As pointed out in section II.A.5, the description of an excited state in the MO format is, with some exceptions, usually wrong and always inaccurate. Rydberg states may well constitute exceptions. Unfortunately, our knowledge of molecular Rydberg states is not massive; in fact, it is so poor that the phenomena which might be interpreted along MO lines have not yet been elaborated experimentally.

In any event, the MO description of excited states will not be as successful as was that for the ground state. Nonetheless, we propose to undertake such a description. In order to evade gross over-simplification and error, we restrict our considerations to weak interactions (i.e., ones for which all off-diagonal blocks of eq 122 are small relative to blocks I, II, III, and IV). Strong interactions imply the inability to compare an MO of AB, other than formally, with those pertinent to either A or B.

We now enumerate various types of excited states and the manner in which they relate to eq 122.

Locally Excited States. This class of states consists of excited electronic states of AB which are not very different from those of fragment A (or fragment B). Thus, even in the composite molecule, they may be described as $\phi^A_{occ,i} \rightarrow \phi^A_{unocc,j}$. In the simplest basis, the transition energy difference caused by the incorporation of A into AB is

$$-\Delta\epsilon^A_{occ,i} + \Delta\epsilon^A_{unocc,j} = -\langle \phi^A_{occ,i} | \mathcal{J}^B + \mathcal{J}^{AB} | \phi^A_{occ,i} \rangle + \langle \phi^A_{unocc,j} | \mathcal{J}^B + \mathcal{J}^{AB} | \phi^A_{unocc,j} \rangle \quad (137)$$

This involves consideration of blocks I and II only.

This empirical classification is quite large. Examples run the gamut from the 4600-Å absorption band of I_2 in various aromatic–iodine complexes,[69] to the effect of solvent–solute adducts on the excited states of solute species.[3c] The 4600-Å band of I_2 is shown in Figure 17. The I_2 forms charge-transfer complexes, I_2·solvent, in the media shown in Figure 17. The energy of the charge-transfer band is quite variable whereas that of the 4600-Å band is subject only to relatively minor variations. The

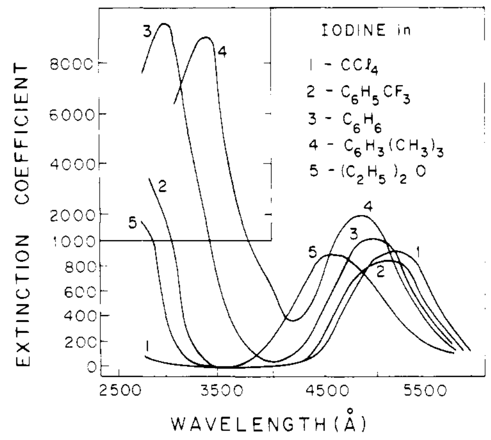


Figure 17. Absorption spectrum of iodine in various solvents. The transition 4000–5000 Å range is characteristic of monomer I_2. The transition which lies below 3500 Å and whose energy is quite variable is the charge-transfer absorption of the I_2·solvent CT complex. This figure is adapted from J. D. Boggus, M.S. Thesis, Florida State University, 1976.

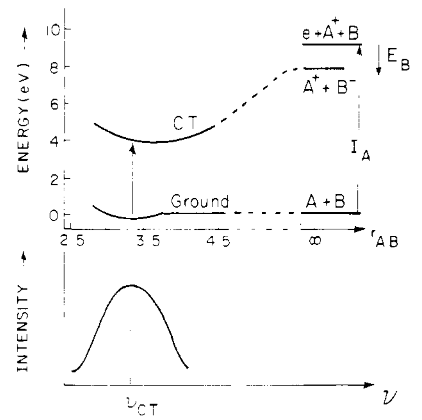


Figure 18. Schematic potential energy diagram (upper) for two states of a charge-transfer complex formed between an acid A and a base B. The ionization potential of the acid (i.e., donor) is denoted I_A and the electron affinity of the base (i.e., acceptor) is denoted E_B. The ground state AB is slightly stable and the resultant CT absorption spectrum of the AB species, which we may approximately denote AB A^+B^-, is shown in the lower diagram. This diagram is adapted from R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

I_2·CCl_4 adduct is very unstable and, while it is often considered to represent a charge-transfer complex, it is best to treat it as a solvent–solute complex of undetermined nature and stoichiometry.

Charge-Transfer Excited States.[69-71] This class consists of excited states of AB which may be categorized as $\phi^{A}_{occ,i} \rightarrow \phi^{B}_{unocc,j}$. This class is dependent, for its existence, on the presence of AB and does not occur in either A or B separately. It is a well-defined class only if $\phi^{A}_{occ,i}$ and $\phi^{B}_{unocc,j}$ do not change much when the composite AB is formed. If no change occurs, we find

$$\begin{aligned} E_{CT} = {} & \epsilon^{B}_{unocc,j} + \langle \phi^{B}_{unocc,j} | \mathcal{F}^{A} + \mathcal{F}^{AB} | \phi^{B}_{unocc,j} \rangle \\ & - \epsilon^{A}_{occ,i} - \langle \phi^{A}_{occ,i} | \mathcal{F}^{B} + \mathcal{F}^{AB} | \phi^{A}_{occ,i} \rangle - \langle \phi^{B}_{unocc,j}(1) \\ & \times \phi^{A}_{occ,i}(2) | [(1 - \mathcal{P}_{12})/r_{12}] | \phi^{B}_{unocc,j}(1) \phi^{A}_{occ,i}(2) \rangle \end{aligned} \tag{138}$$

which, by Koopmans' theorem, is

$$E_{CT} = -EA^{B} + IE^{A} + C \tag{139}$$

where *C* contains all remaining terms, particularly those which are coulombic.

This empirical classification is very large. Extensive examples are available in Mulliken and Person.[69] This categorization also includes "charge transfer to solvent" or CTTS states.[69] All evolve from the truncated secular equation

$$\begin{vmatrix} \text{II} & \text{VIIa} \\ \text{VIIa} & \text{IV} \end{vmatrix} = 0 \tag{140}$$

The potential energy curves for the ground and CT excited state of a charge-transfer complex are shown in Figure 18. The ground state has a small but finite stabilization energy which is greater than kT_0. The excited state, relative to dissociation into A^+ and B^-, possesses considerable stabilization energy. The charge-transfer absorption band of certain I_2 complexes is also shown in Figure 17.

When a composite molecule is built from two (nearly) identical bits A and B, one immediately runs into problems concerned with approximate spatial degeneracy, as discussed in section II.A.5.c. For example, in the charge-transfer case, the description $\phi^{A}_{occ,i} \rightarrow \phi^{B}_{unocc,j}$ is no longer unique; the (almost) equally probable situation $\phi^{B}_{occ,i} \rightarrow \phi^{A}_{unocc,j}$ must have (nearly) equal weight in any final description of the charge-transfer transition. However, in the most simple cases, one can still reduce the description to separate interactions which occur solely within the occupied and solely within the unoccupied MO subsets of the two bits. We will now discuss two such cases.

Rydberg States of Composite Systems. Although such an approach is fairly alien to Rydberg spectroscopy, the orbital interaction picture can be extended to systems containing two identical Rydberg chromophores. The energy of a Rydberg transition, under these conditions, is given by

$$h\nu^{AB} = IE^{AB} + \tilde{\epsilon}^{A}_{R} + \Delta E \tag{141}$$

where, from blocks I, IV, and VIII of eq 122

$$\begin{aligned} \Delta E = {} & \langle \phi^{A}_{R} | \mathcal{F}^{B} + \mathcal{F}^{AB} | \phi^{A}_{R} \rangle \\ & \pm (1 \pm S)^{-1} [2\tilde{\epsilon}^{a}_{R} S + \langle \phi^{A}_{R} | \mathcal{F}^{AB} | \phi^{B}_{R} \rangle] \end{aligned} \tag{142}$$

and where the overlap integral is

$$S = \langle \phi^{A}_{R} | \phi^{B}_{R} \rangle \tag{143}$$

In addition, using blocks II, III, and V, the ionization energy of the composite system can be related to those of the bits A and B. This approach has been used to discuss the energies, dipole selection rules, and lengths of certain Rydberg series in the α-dicarbonyls.[72]

Excimer States.[73-75] Excimer states are stable excited states of a dimer, A_2^*, which is dissociative in its ground state, A_2. The idea of an excimer is exemplified in Figure 19. If A ≠ B, the associated excited state entity (AB)* is known as an "exciplex".[76] If A = B and if the excited state entity A_n^* is part of an ordered structure in which *n* is very large, the entity A_n^* is known as an "exciton".[77] Exciplexes are of common occurrence in photoexcited solutions. Excitons provide a simple description of the excited states of molecular crystals.[78]

As is already obvious from our language, the discussion of excited states of a molecule AB in terms of those of the bits A and B is usually processed in valence bond (VB) language.[78] Thus, Mulliken,[69] in his discussion of charge-transfer complexes, introduces electron configurations with names such as "no-bond", "locally-excited", "charge transfer", and "retro-charge transfer". Thereafter, he describes the electronic states of such complexes on the basis of a configuration mixing among these various electron structures (i.e., no-bond, charge transfer, etc.). A similar situation prevails in almost all discussions of excited-state properties of composites AB. In fact, the status of this whole area is peculiar: the interaction concepts are best elaborated on a VB basis whereas computations are best prosecuted on a "super-molecule" (i.e., AB) MO basis.

Unfortunately, the relation of the MO results to the VB concepts is rarely straightforward. In fact, it usually devolves on an analysis of one set of results, namely the MO computations, in terms of the concepts of the other, namely the VB, in order to

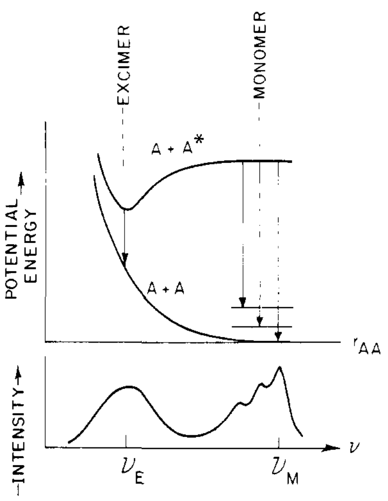


Figure 19. A schematic potential energy diagram (upper) for an excimer. These curves describe the energetics of approach of two A molecules, say two naphthalene molecules (in which case r_{AA} is the interplanar distance as the two naphthalenes approach along a joint D_{2h} symmetry axis). The excited monomer is denoted A*. The monomer emission is A* → A and the excimer emission is AA* → 2A. The ground state is repulsive and the excited state is attractive. A schematic emission spectrum (lower) of a system which forms excimers and for which both the monomer M and the excimer E are emissive. The monomer emission, as shown, possesses vibronic structure. This diagram is adapted from B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, **60,** 1515 (1964).

validate the preconceptions of the latter.

In order to put our finger on the difficulties that arise, we will now process a simple model within both the valence bond and molecular orbital frameworks. *Our model system contains two bits A and B, and each bit contains just one electron. We neglect both overlap and spin. The orbital basis consists of only one occupied and one unoccupied orbital for each of the bits A and B.*

Valence Bond Approach. The most simple description of ground and excited states is given by the following set of determinants:

$$\psi_0 = |\phi^A_{occ}\phi^B_{occ}| \tag{144}$$

$$\psi_{BA^*} = |\phi^A_{unocc}\phi^B_{occ}| \tag{145a}$$

$$\psi_{AB^*} = |\phi^A_{occ}\phi^B_{unocc}| \tag{145b}$$

$$\psi_{BB^*} = |\phi^B_{unocc}\phi^B_{occ}| \tag{145c}$$

$$\psi_{AA^*} = |\phi^A_{occ}\phi^A_{unocc}| \tag{145d}$$

where ψ_0 represents the ground states; ψ_{AA^*} and ψ_{BB^*} represent charge-transfer and ψ_{AB^*} and ψ_{BA^*} locally excited states. For obvious reasons, the locally excited configurations are considered to be nonpolar, and the charge-transfer configurations are considered to be polar. If the two bits are identical, one is forced to take linear combinations of the two locally excited and the two charge-transfer configurations. Excimer states, for instance, may be described by

$$\Psi_{\pm} = 2^{-1/2}(\psi_{BA^*} \pm \psi_{AB^*}) \tag{146}$$

Molecular Orbital Approach. The simple MO approach to the same problem starts with the set of symmetry-adapted functions

$$\phi_+^{AB} = \frac{1}{\sqrt{2}}(\phi^A_{occ} + \phi^B_{occ}) \tag{147a}$$

$$\phi_-^{AB} = \frac{1}{\sqrt{2}}(\phi^A_{occ} - \phi^B_{occ}) \tag{147b}$$

$$\phi_+^{A^*B^*} = \frac{1}{\sqrt{2}}(\phi^A_{unocc} + \phi^B_{unocc}) \tag{147c}$$

$$\phi_-^{A^*B^*} = \frac{1}{\sqrt{2}}(\phi^A_{unocc} - \phi^B_{unocc}) \tag{147d}$$

Ground and excited states are now described by

$$\psi_0 = |\phi_+^{AB}\phi_-^{AB}| \tag{148}$$

$$\psi_1 = |\phi_+^{A^*B^*}\phi_-^{AB}| \tag{149a}$$

$$\psi_2 = |\phi_+^{AB}\phi_-^{A^*B^*}| \tag{149b}$$

$$\psi_3 = |\phi_-^{A^*B^*}\phi_-^{AB}| \tag{149c}$$

$$\psi_4 = |\phi_+^{AB}\phi_+^{A^*B^*}| \tag{149d}$$

The ground configuration is identical with that of the VB format.[14] The excited configurations, however, represent linear combinations of VB configurations, namely

$$\psi_1 = \frac{1}{2}(\psi_{AA^*} + \psi_{BB^*} + \psi_{AB^*} + \psi_{BA^*}) \tag{150a}$$

$$\psi_2 = \frac{1}{2}(\psi_{AA^*} + \psi_{BB^*} - \psi_{AB^*} - \psi_{BA^*}) \tag{150b}$$

$$\psi_3 = \frac{1}{2}(\psi_{AA^*} - \psi_{BB^*} - \psi_{AB^*} + \psi_{BA^*}) \tag{150c}$$

$$\psi_4 = \frac{1}{2}(\psi_{AA^*} - \psi_{BB^*} + \psi_{AB^*} - \psi_{BA^*}) \tag{150d}$$

The set of MO configurations $\{\psi_0, \psi_1, \ldots \psi_4\}$ obviously spans the same space as the set of VB configurations $\{\psi_0, \psi_{AA^*}, \psi_{BB^*}, \psi_{AB^*}, \psi_{BA^*}\}$. Each singly excited MO configuration, however, contains 50% polar (charge-transfer) and 50% nonpolar (locally excited) character, whereas the configurations of the VB set are either 100% nonpolar or 100% polar.

Unfortunately, the actual states probably cover the full range from 100% polar to 100% locally excited. Generally, neither the simplistic MO nor the simplistic VB approach (which uses only one configuration function) will give an adequate picture, and one is forced to use a multideterminantal description. This requirement, of course, can be traced back to the nonexistence of a Koopmans' theorem for electron excitation, as discussed in sections II.A.5.a and c.

A case for which the matrix elements of blocks V, VI, and VIII are of importance is provided by the n → π* transitions of tetramethylcyclobutane-1,3-dione (TMCBD). The splitting of the n_O orbitals is 0.53 μm^{-1} (PES), that of the π* orbitals is 0.05 μm^{-1} (CNDO), and the four observed n → π* singlet states cover a range of 0.9 μm^{-1} (VIS, UV). The absoption spectrum is shown in Figure 20. The apparent complexity of this situation can be attributed to configuration interaction, mainly within the n → π* manifold, and to deficiencies of the CNDO algorithm. In any event, instead of a single n → π* transition (cf. the 2700-Å transition of acetone), one expects and observes four n → π* transitions in TMCBD. The origin of these four n → π* transitions is schematized on an MO basis in Figure 21. We hope, by this example, to have fleshed out the abstract conclusions of section II.A.5 in a more relevant frame of reference.

C. Realm, Merits, and Limits

The orbital interaction picture is an especially good approximation when the experimental data are ionization energies (such energies, via Koopmans' theorem, refer directly to orbital energies); one of the off-diagonal elements is very large compared to all others; one or two of the orbital energies of both A and B are well separated from the remainder (if these bunched MO's are the ones which interact, the influence of the other orbitals will be small because of the large energy denominators which will occur in the perturbation theory expressions); high symmetry prevails (this forces a lot of matrix elements to zero); the experimental information is incomplete! (Lacking sufficient

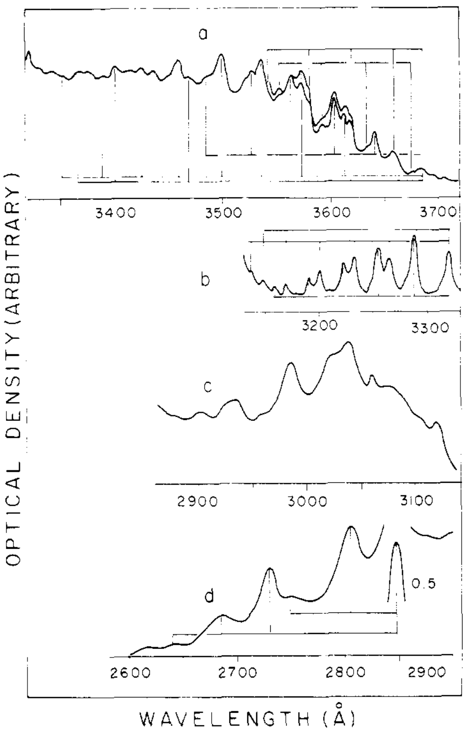


Figure 20. The absorption spectrum of TMCBD (thin polycrystalline film) at 77 K. Four n → π^* transitions are observed in the region 3700–2600 Å. These are shown individually and tentative vibronic analyses are schematized for three of them. This spectrum is taken from work by P. Brint (LSU, unpublished).

information, one can subsume all kinds of unknown interactions into one or two types and parameterize accordingly.)

The success of the orbital interaction approach is well documented in the literature, and it accounts for the popularity of both photoelectron spectroscopy and the application of MO theory to chemistry.

Total electronic energies, however, involve summations over all the occupied orbitals, and it is difficult to see how such total energies can be decomposed into one or even a few crucial orbital contributions. Hence, the orbital interaction concepts are best relegated to discussions of phenomena which can be pursued, with some force of logic, at the orbital level (e.g., PES). Such concepts, when applied to total energies or excited state properties, must be processed warily because the necessary logic apparatus (i.e., Koopmans' theorem) does not exist.

The formal description of orbital interactions is clear-cut and simple. The difficulty (or the art) of application of the orbital interaction concepts to an actual problem lies, on the one hand, in the definition of the parent systems and, on the other hand, in the definition of the interaction operator, $\mathcal{F}^{AB}$. Our definition of $\mathcal{F}^{AB}$, as given in eq 118, requires a knowledge of the Fock operators for the bits as well as the composite system. This, in turn, implies a knowledge of the electron distributions in all three of A, B, and AB. Once these distributions are known, calculation of the orbital energies is straightforward.

The primary virtue of orbital interaction concepts, apart from their simplicity, lies in the arbitrariness of the definitions[79] of $\mathcal{F}^{A}$, $\mathcal{F}^{B}$, and $\mathcal{F}^{AB}$. Thus, it is not unusual that the only information which can be deduced from experiment consists of the types and, perhaps, the magnitudes of several of the matrix elements. Although some consistency can be achieved with respect to certain definitions (e.g., the choice of $\mathcal{F}^{A}$ and $\mathcal{F}^{B}$) and with respect to the empirical values of certain of the interaction matrix elements, the significance of either the axiomatic or the numerical precision will usually be severely limited.[80] First, the MO concept is inherently approximate; for example, electronic relaxation and correlation effects are not properly taken care of even in the case of ionization energies. These approximations are of such a nature that they have different effects on different parameters, as witness the fact that the value of the same parameter deduced from different types of experimental data can vary quite widely. Secondly, the set of approximations involved in the evolution of the orbital interaction classification (i.e., neglect of specific matrix elements; the choice of ϕ^A, ϕ^B, and ϕ^{AB}; etc.) is not unique. Consequently, the numerical values of the "same" parameter deduced by different authors from the same data set are liable to differ considerably. Despite all of this, it is nonetheless true that the orbital interaction scheme has proven invaluable in the development, application, and analysis of both semiempirical and nonempirical MO calculations.

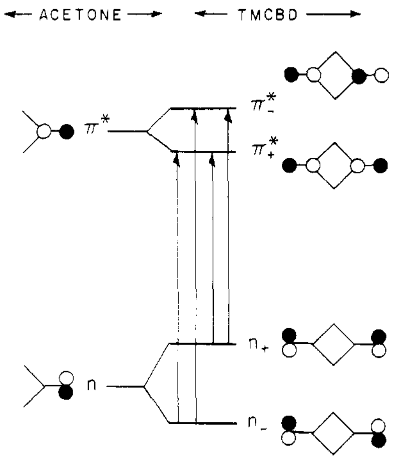


Figure 21. The n and π^* MO's of acetone (left) and TMCBD (right), indicating the reasons for the four expected n → π^* transitions of the latter.

We have worked implicitly and explicitly at the Hartree–Fock level. Since the errors inherent in the MO approximation may be very large compared to the difference between Hartree–Fock and "near-Hartree–Fock" calculations, we see little sense in the search for a perfect numerics. Thus, minimal basis set ab initio or semiempirical MO calculations have been and will remain extremely useful. The success of the semiempirical schemes is attributable to two factors. First, it is due to the nonpolar nature of the general run of molecules which has been considered. This nonpolarity guarantees that a Mulliken–Wolfsberg–Helmholtz type of approximation should be reasonably correct. Secondly, it is due to the unspecified nature of the basis set. These two factors imply that all semiempirical MO methods, despite their apparently numerical nature, rest on precisely the same foundations as the orbital interaction concepts.

IV. Conclusion

Quantum chemistry is faced with two fundamental problems: how to reduce chemistry, in a practical way, to numerics; and how to avoid doing so and still benefit from theory. We have spoken to the latter problem in this article. The situation with respect to the former is in considerable flux because of the increasing sophistication of computers and programs.

The axiomatic foundations of MO theory are well settled. Although different semiempirical MO versions will come and go and new types of orbital interactions will be advanced, it is doubtful that the MO concepts will alter radically. There is a possibility, however, that the MO terminology will be supplemented, improved, or even replaced by concepts originating in atomic, solid-state, and nuclear physics. The impact of some such concepts on chemistry has already been investigated, and we feel it imperative to mention a few of the more important of them.

Xα Calculations.[81] These calculations use an approximation for the exchange integral which is of the form

$$V_{X\alpha\uparrow}(1) = -6\alpha[3/4\pi]^{1/3}[\rho\uparrow(1)]^{1/3} \tag{151}$$

where $\rho\uparrow$ is the electron density for "spin-up" and α is a parameter which is adjustable within the limits $1 \leq \alpha \leq 2/3$. The "muffin tin" approximation, which describes the individual atom regions as regions of spherical potential, is used heavily. The impact on chemistry may be a replacement, or a modification of the LCAO format as we presently know it.

Pseudopotential Theory.[82] The pseudopotential idea permits an exact treatment of one or a few electrons which move in a potential provided by all the other electrons and the nuclei. It promises to be an exceedingly powerful approach for loosely bound electrons (e.g., electrons in Rydberg states). It provides a simple means of evading the many problems which arise when dealing with large numbers of core electrons as, for example, in heavy-metal compounds. Since it is the core electrons which furnish most of the electronic energy of such compounds, the pseudopotential theory, by including them in the potential term, enables one to focus more precisely on the small energy differences associated with the valence states.

Second-Quantization and Green's Function Method.[83,84] There is reason to expect that new concepts will arise either from the diagrammatic or from the propagator approaches. The main difficulty, for the time being, resides in their unfamiliarity to chemists.

Relativistic Calculations. Truly relativistic calculations are still rare for molecules. There is reason to expect that such calculations will have a considerable impact on heavy-metal chemistry.

We have concentrated on the MO idea: on how to describe the motion of an electron in the average field of a complicated system; on where the MO idea is valid and, hence, useful; and on where it breaks down. We admit that the MO idea fails numerically. Nevertheless, it has been *the* unifying approach in chemistry and molecular spectroscopy for the last 30 years. And it remains so today. We feel compelled to stress the centrality of Koopmans' theorem and the manner in which it allows us to attach a physical meaning to the concepts of orbitals and orbital energies. We also feel compelled to emphasize the practicality of orbital interaction concepts. Although no new types of physical interactions are introduced, ($\mathcal{F}$, after all, contains terms only for kinetic and coulombic energies), it supplies a set of simple ideas which are qualitatively useful in an area where numerical efforts fare rather badly.

In sum, we have justified the orbital description of ionization and excitation processes, irrespective of whether the electron is strongly coupled to one nucleus, (i.e., a core electron), loosely coupled to the whole molecule (i.e., a Rydberg electron), or moderately coupled to all atoms of the whole molecule (i.e., a valence electron). The primary limitations are ones imposed by symmetry restrictions, space as well as spin, and by the very silly but very human endeaver to extract physical and numerical exactitude from an approximate theory.

V. References

(1) Although identical in a linguistic sense, the term "electron spectroscopy" has acquired a different meaning from the term "electronic spectroscopy". We will use the latter term when we deal with processes involving transitions among different electronic states of an *N*-electron system. Electron spectroscopy, on the other hand, refers to ionization processes.

(2) (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970; (b) J. H. D. Eland, "Photoelectron Spectroscopy", Butterworths, London, 1974; (c) J. W. Rabalais, "Principles of Ultraviolet Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1977; (d) K. Siegbahn, C. Nordling, A. Fahlmann, R. Nordberg, K. Hamrin, J. Hedman, C. Johansson, T. Bergmark, S. E. Karlson, I. Lindgren, and B. Lindberg, "ESCA. Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy", Ser. IV, Almquist and Wiksells, Uppsala, 1967, p 20; (e) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and U. Baer, "ESCA Applied to Free Molecules", North Holland, Amsterdam, 1969; (f) T. H. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, N.Y., 1975.

(3) Of the many excellent texts available on molecular electronic spectroscopy, we mention but a few: (a) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Wiley, New York, N.Y., 1963; (b) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967; (c) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra", Marcel Dekker, New York, N.Y., 1970; (d) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, New York, N.Y., 1969.

(4) We refrain from listing specific examples. We do not intend our remarks to be derogatory. In order to provide a proper insight to the principles of quantum theory and the applications of quantum chemistry, so much effort has to be invested that the aspects we wish to emphasize in this article usually receive no more than token treatment.

(5) The other important method of excitation uses electrons; the book by Christophorou (L. G. Christophorou, "Atomic and Molecular Radiation Physics", Wiley-Interscience, New York, N.Y., 1971) provides an excellent introduction to electron excitation methods.

(6) We use atomic units in all equations.

(7) For a fuller discussion, see J. C. Slater, "The Quantum Theory of Molecules and Solids. I. Electron Structure of Molecules", McGraw-Hill, New York, N.Y., 1963.

(8) The actual Born-Oppenheimer approximation uses $\Psi_{el}(\mathbf{x};\mathbf{R}_0)$ as opposed to the specification given here. We have used the so-called "adiabatic" approximation. The differences become important for various perturbative schemes. See, for example, R. Englman, "The Jahn-Teller Effect in Molecules and Crystals", Wiley-Interscience, New York, N.Y., 1972.

(9) An orbital—whether atomic, molecular, canonical, localized, or otherwise—is strictly a one-electron function. A spin orbital, in contrast to a space orbital, depends on spin and space coordinates. We prefer the unrestricted Hartree-Fock formalism; hence, we will usually work in a spin-orbital context.

(10) That is, $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$.

(11) A configuration specifies the set of "occupied" orbitals. For closed shell systems, each configuration corresponds to one single determinant.

(12) This, of course, is our definition of "best". One could equally well seek that determinant which would, in a least-squares sense, reproduce the electron density as closely as possible. This turns out to be a much more formidable problem.

(13) See, for example, H. Watanabe, "Operator Methods in Ligand Field Theory", Prentice-Hall, Englewood Cliffs, N.J., 1966.

(14) As an example, consider a two-electron system for which

$$\psi = (1/2)^{1/2}\begin{vmatrix}\varphi_1(1) & \varphi_2(1)\\ \varphi_1(2) & \varphi_2(2)\end{vmatrix} = (1/2)^{1/2}[\varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1)]$$

If we define

$$\varphi_+ \equiv (1/2)^{1/2}(\varphi_1 + \varphi_2)$$
$$\varphi_- \equiv (1/2)^{1/2}(\varphi_1 - \varphi_2)$$

we obtain

$$\begin{aligned}\psi' &= (1/2)^{1/2}\begin{vmatrix}\varphi_+(1) & \varphi_-(1)\\ \varphi_+(2) & \varphi_-(2)\end{vmatrix}\\ &= (1/2)^{1/2}[\varphi_+(1)\varphi_-(2) - \varphi_+(2)\varphi_-(1)]\\ &= (1/8)^{1/2}\{[\varphi_1(1) + \varphi_2(1)][\varphi_2(2) - \varphi_1(2)] - [\varphi_1(2) + \varphi_2(2)][\varphi_2(1) - \varphi_1(1)]\}\\ &= (1/8)^{1/2}[\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2) - \varphi_1(2)\varphi_2(1) + \varphi_2(2)\varphi_1(1)]\\ &= (1/2)^{1/2}[\varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1)] = \psi\end{aligned}$$

(15) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32,** 179 (1960).

(16) B. Solouki, P. Rosmus, and H. Bock, *J. Am. Chem. Soc.*, **98,** 6054 (1976).

(17) W. Meyer, *Int. J. Quant. Chem.*, **55,** 341 (1971); *J. Chem. Phys.*, **58,** 1017 (1973).

(18) See p 84 of ref 3d.

(19) M. B. Robin, "Higher Excited States of Molecules", Vol. I and II, Academic Press, New York, N.Y., 1971.

(20) H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules. A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.

(21) H. Bock and B. G. Ramsey, *Angew. Chem.*, **85,** 773 (1973); *Angew. Chem., Int. Ed.*, **12,** 734 (1973).

(22) T. Koopmans, *Physica*, **1,** 104 (1933).

(23) This second part elevates Koopmans' theorem from the status of a mere algebraic identity to that of a theorem. This development is given in Koopmans' original paper. However, we have chosen to follow the more explicit treatment of M. D. Newton, *J. Chem. Phys.*, **48,** 2825 (1968).

(24) Atomic electron affinities are reviewed by H. Hotop and W. C. Linneberger, *J. Phys. Chem. Ref. Data*, **4,** 539 (1975).

(25) A discussion of this aspect is given by W. L. Smith, *Mol. Phys.*, **26,** 361 (1973).

(26) For a use of Koopmans' theorem including spin-orbit coupling, see K. Wittel, *Chem. Phys. Lett.*, **15,** 555 (1972); R. Manne, K. Wittel, and B. S. Mohanty, *Mol. Phys.*, **29,** 485 (1975).

(27) M. Jungen, *Theor. Chim. Acta*, **27,** 33 (1972).

(28) One such example is provided by the fluorine molecule, F_2. The "best" calculation provides the MO sequence π_g, σ_g, π_u: A. C. Wahl, *J. Chem.*

Phys., **41,** 2600 (1964). However, the sequence of cationic states, as obtained from rotational analysis of the $^2\Pi_u \rightarrow {}^2\Pi_g$ emissive transition of F_2^+ [T. L. Porter, *J. Chem. Phys.*, **48,** 2071 (1968).] is $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_g$.

(29) C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53,** 2196 (1972).

(30) C. Fridh, L. Asbrink, and E. Lindholm, *Chem. Phys. Lett.*, **15,** 282 (1972).

(31) A discussion of the relative importance of the coulomb and exchange terms for different electronic transitions of the same molecule can be found in E. Haselbach and A. Schmelzer, *Helv. Chim. Acta*, **54,** 1975 (1971); **55,** 1945 (1972); C. Batich, E. Heilbronner, E. Rommel, M. F. Semmelhack, and J. S. Foos, *J. Am. Chem. Soc.*, **96,** 7662 (1974).

(32) F. A. Matsen, *J. Am. Chem. Soc.*, **92,** 3525 (1970), and references given therein.

(33) That this is not necessarily the case is demonstrated in R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **36,** 415 (1975).

(34) This treatment follows closely that of W. F. Hunt and W. A. Goddard, *Chem. Phys. Lett.*, **3,** 414 (1969). These authors give separate equations for singlet and triplet states.

(35) For an extensive discussion, see (a) M. B. Robin, "Higher Excited States of Molecules", Vol. I and II, Academic Press, New York, N.Y., 1975; (b) A. B. F. Duncan, "Rydberg Series in Atoms and Molecules", Academic Press, New York, N.Y., 1971.

(36) See ref 35a, Vol. I, p 51.

(37) The term "core orbitals", as used in this section, comprises the set of occupied orbitals of the cationic state to which a Rydberg series converges. Thus, "core" in this section consists of both the valence and inner-shell regions. No confusion should arise with respect to the usage "core" ≡ "inner shells" in section II.C and elsewhere.

(38) R. S. Mulliken, *J. Am. Chem. Soc.*, **86,** 3183 (1964); **88,** 1849 (1966); **91,** 4615 (1969).

(39) (a) A. Sommerfeld, "Atombau and Spektrallinien", Vol. II, F. Vieweg and Sohn, Braunschweig, New Printing, 1953, p 140; (b) L. D. Landau and E. M. Lifshitz, "Quantum Mechanics: Non-Relativistic Theory", 2nd ed, Pergamon Press, New York, N.Y., 1965, p 123.

(40) The Xα method used just such a local exchange potential: J. C. Slater, "The Quantum Theory of Molecules and Solids", McGraw-Hill, New York, N.Y., 1976.

(41) U. Gelius, B. Roos, and P. Siegbahn, *Chem. Phys. Lett.*, **4,** 471 (1970); F. O. Ellison and L. L. Larcom, *ibid.*, **10,** 580 (1971).

(42) In the early days of XPS, the charging of nonconducting samples during the course of a measurement caused much difficulty because of band broadening and ill-defined calibration points.

(43) A discussion of this aspect is contained in T. A. Carlson, J. C. Carver, L. J. Seathre, F. Garcia-Santibauer, and G. A. Vernon, *J. Electron Spectrosc.*, **5,** 247 (1974); "Electron Spectroscopy. Proceedings of an International Conference on Electron Spectroscopy", held in Namur, April 16–19, 1974, R. Caudano and J. Verbist, Ed., Elsevier, Amsterdam, 1974.

(44) This derivation follows that of R. Manne, Winter Institute of Theoretical Chemistry, Spätind, Norway, 1973.

(45) (a) P. Politzer and P. H. Reggio, *J. Am. Chem. Soc.*, **94,** 8308 (1972); (b) P. Baybutt, W. N. E. Meredith, M. F. Guest, V. R. Saunders, I. H. Hillier, J. A. Conner, and M. Barber, *Mol. Phys.*, **25,** 1011 (1973).

(46) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **10,** 378 (1971).

(47) The derivation follows R. Manne and T. Aberg, *Chem. Phys. Lett.*, **7,** 282 (1972).

(48) The symbol "*i*", as used here, is merely a numbering subscript. It does not refer to any orbital in particular.

(49) This development is analogous to the Franck–Condon principle for electronic transitions. This principle states that the electronic transition is not accompanied, immediately anyway, by a change of nuclear coordinates. Thus, we write the transition as

$$\Psi_i(\mathbf{x};\mathbf{R}_0)\Xi_i(\mathbf{R}) \rightarrow \Psi_f(\mathbf{x};\mathbf{R}_0)\Xi_i(\mathbf{R})$$

where i denotes "initial" and f denotes "final" and where, according to Franck-Condon, $\Xi_i(\mathbf{R})$ does not change. Now, $\Xi_i(\mathbf{R})$ is not an eigenfunction of the nuclear Hamiltonian for the excited state. However, $\Xi_i(\mathbf{R})$ can be expanded in terms of the set of eigenfunctions of the nuclear Hamiltonian for this excited state

$$\Xi_i(\mathbf{R}) = \sum_k \Xi_{fk}(\mathbf{R})C_{ki}$$

where

$$C_{ki} = \langle \Xi_i(\mathbf{R}) | \Xi_{fk}(\mathbf{R}) \rangle_{\mathbf{R}}$$

The relative transition probabilities to different vibrational levels of the final state are proportional, therefore, to the squares of the corresponding Franck-Condon factors, C_{ki}^2.

(50) Again, the analogy to the Franck-Condon idea is obvious; see W. L. Smith, ref 25 above.

(51) R. Manne, *J. Chem. Phys.*, **52,** 5733 (1970); *J. Phys.*, **32,** C4-151 (1971); G. Karlson and R. Manne, *Phys. Scr.*, **4,** 119 (1971).

(52) M. Klasson and R. Manne in "Electron Spectroscopy", D. A. Shirley, Ed. North-Holland, Amsterdam, 1972, p 471; R. Manne, *Chem. Phys. Lett.*, **5,** 125 (1970).

(53) K. Wittel, E. E. Astrup, H. Bock, G. Graeffe, and H. Juslen, *Z. Naturforsch., Teil B*, **30,** 862 (1975).

(54) W. H. E. Schwarz, *Chem. Phys.*, **11,** 217 (1975).

(55) The difference between "one-electron" and "one-orbital" properties should be noted.

(56) L. C. Cusachs, *J. Chem. Phys.*, **43,** S157 (1965).

(57) K. Fukui, *Fortschr. Chem. Forsch.*, **15,** 1 (1970).

(58) See, for example, K. Wittel and H. Bock, *Chem. Ber.*, **107,** 317 (1974).

(59) A variety of examples are discussed in ref 2c and 17.

(60) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56,** 1028 (1973).

(61) (a) T. P. Debies and J. W. Rabalais, *J. Electron Spectrosc.*, **1,** 355 (1972/73); (b) S. A. Cowling and R. A. W. Johnstone, *Faraday Discuss.*, **54,** 197 (1972).

(62) E. Heilbronner, *Isr. J. Chem.*, **10,** 143 (1972).

(63) H. Bock and W. Ensslin, *Angew. Chem.*, **83,** 435 (1971); *Angew. Chem. Int. Ed. Engl.*, **10,** 404 (1971).

(64) E. Heilbronner and K. Muszkat, *J. Am. Chem. Soc.*, **92,** 3818 (1970).

(65) R. Hoffman, *Acc. Chem. Res.*, **4,** 1 (1971).

(66) Data for norbornane, norbornene, and norbornadiene are contained in P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52,** 1745 (1969).

(67) K. Wittel, A. Hass, and H. Bock, *Chem. Ber.*, **105,** 3865 (1972).

(68) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96,** 1370 (1974).

(69) R. S. Mulliken and W. B. Person, *Annu. Rev. Phys. Chem.*, **13,** 107 (1962); "Molecular Complexes", Wiley-Interscience, New York, N.Y., 1969.

(70) S. Nagakura, "Excited States," Vol. II, E. C. Lim, Ed., Academic Press, New York, N.Y., 1972, p 321.

(71) Complexes which are stable in the ground state possess a stabilization energy $\Delta E_0 \geq kT$. If $kT > \Delta E_0 \geq 0$, the "complex" is known as a "contact complex". Exciplexes, by definition, have $\Delta E_0 < 0$.

(72) P. Brint, K. Wittel, W. S. Felps, P. Hochmann, and S. P. McGlynn, *J. Am. Chem. Soc.*, **98,** 7980 (1976).

(73) J. B. Birks, *Rep. Prog. Phys.*, **38,** 903 (1975).

(74) S. P. McGlynn, A. T. Armstrong, and T. Azumi in "Modern Quantum Theory", Vol. III, O. Sinanoglu, Ed., Academic Press, New York, N.Y., 1965, p 203.

(75) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **38,** 2773 (1963); **39,** 1186 (1963); **41,** 3131 (1964); **42,** 1675 (1965).

(76) An exciplex is an electronically excited atomic or molecular complex of definite geometry which is dissociative or dissociated in its electronic ground state. The stoichiometry is usually 1:1, but triple (or 2:1) exciplexes have been observed. An excimer, then, is a 1:1 homopolar exciplex between identical atoms or molecules. For further detail see: H. A. Beens and A. Weller, *Chem. Phys. Lett.*, **2,** 140 (1968); "Organic Molecular Photophysics", Vol. II, J. B. Birks, Ed., Wiley-Interscience, New York, N.Y., 1975, p 159.

(77) A. S. Davydov, "Theory of Molecular Excitons", Plenum Press, New York, N.Y., 1971; R. Kopelman in "Excited States, II", E. C. Lim, Ed., Academic Press, New York, N.Y., 1975, p 33.

(78) S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry", Holt-Rinehart and Winston, New York, N.Y., 1972, Chapter 6.

(79) Two ethylenes differ from butadiene by two hydrogen atoms. Consequently, the definition of the bits A and B obviously involves a degree of ambiguity.

(80) Interaction matrix elements derived from several closely related semiempirical MO calculations may differ not only in magnitude, but also in *sign*. Any intense effort to obtain the corresponding numbers with high reliability and high accuracy from experimental data is therefore liable to fail; see E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, **58,** 936 (1975).

(81) See J. C. Slater, ref 40.

(82) J. D. Weeks, A. Hazi, and S. A. Rice, *Adv. Chem. Phys.*, **16,** 283 (1969).

(83) J. Linderberg and Y. Öhrn, "Propagators in Quantum Chemistry", Academic Press, London, 1973.

(84) J. Paldus and J. Cizek, *Adv. Quant. Chem.*, **9,** 105 (1975).

(85) Although a vertical ionization energy is well defined, the concept of a vertical transition, when carried to the extreme, encounters problems connected with the Heisenberg uncertainty principle. See, for example, S. E. Schwartz, *J. Chem. Educ.*, **50,** 608 (1973).