is treated as if the single aromatic system containing triplet excitation suddenly jumps to the orientation of the system which receives the excitation. Although his interpretation probably does not include important components of the phenomenon, it yields a remarkably satisfactory account of the temperature dependence of the spectra.

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Ab Initio Studies of Molecules and Concepts of Molecular Structure

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For more than a decade much effort has been devoted to the construction of electronic wave functions by so-called *ab initio* techniques with the hope that the predictive capabilities of quantum mechanics could be realized for atoms and molecules.

For this purpose, wave functions and energies usually are determined by energy-variational calculations since the Schrödinger equation is not amenable to direct solution. Conventionally self-consistent-field (SCF) or configuration interaction (CI) formulations have provided the main routes toward approximate solutions. The single-determinant of orbitals form of the total wave function, which is most frequently used in SCF theory, cannot in principle lead to an exact solution, while a CI construction can in principle, but only in the unattainable limit of a complete basis set. Thus, at the levels applied in practice, both methods are imperfect formulations of the many-electron problem. The terminology *ab initio,* as generally used, thus has become associated with the fact that interactions, usually in the form of integrals, are evaluated accurately. It does not mean that the form of the wave function itself is not unduly constrained.

This Account examines some of the main ideas of many-electron theory, discusses some of the successes of computations and some of the uncertainties and failures, and hopefully provides some insight into how some of the *ab initio* conclusions can be incorporated into qualitative lines of reasoning.[1]

Many-Electron Orbital Theory Assumptions

If the dynamics of nuclear motion is not of interest, the nuclei can be considered fixed in space at some chosen geometry which can later be varied (Born–Oppenheimer approximation), giving the Hamiltonian

$$H = \underbrace{\sum_{i}^{N} -\tfrac{1}{2}\nabla_i^{2}}_{\text{el kinetic energy}} + \underbrace{\sum_{i}^{N}\sum_{k}^{M} -\frac{Z_k}{r_{ik}}}_{\text{el–nuc attraction}} + \underbrace{\sum_{i<j}^{N}\frac{1}{r_{ij}}}_{\text{el–el repulsion}} + \underbrace{\sum_{k<l}^{M}\frac{Z_kZ_l}{R_{kl}}}_{\text{nuc–nuc repulsion}} + \underbrace{H'}_{\text{other interactions}}$$

where i and j label the N electrons and k and l label the M nuclei. Contributions, H', due to magnetic interactions or external fields, if sufficiently small, can be neglected in determining the electronic structure, and this assumption is made here. The problem is to solve the Schrödinger equation, $H\Psi_k = E\Psi_k$, for the antisymmetric state functions. For many-electron systems, a direct attack on the differential equation has not led to sufficiently accurate approximations.

This difficulty can be resolved by translating the problem into an equally valid integral form, the energy-variational principle, $E_{\text{exact}} \leq E = \langle\Psi|H|\Psi\rangle$, for ground states, and under known conditions for excited states as well. Wave functions and energies can now be determined by minimizing the average value of the energy of the system with respect to variations of Ψ. The orbital approach has been the most fruitful, both to determine the simplest approximation and to establish a starting point for refinements of Ψ. Its origins can be traced to a crucial approximation, that of replacing the real electron–electron potential by an effective independent particle potential. If this is done, the exact solutions of the modified problem can be expressed either as a simple product of spin orbitals or as a single Slater determinant,[2] $\Psi = \det(\chi_1(1)\chi_2(2)\ \ldots\ \chi_N(N))$, the latter

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(1) A recent survey of *ab initio* quantum mechanical calculations is contained in H. F. Schaefer, III, "The Electronic Structure of Atoms and Molecules," Addison-Wesley, Reading, Mass., 1972.

(2) J. C. Slater, *Phys. Rev.*, **34**, 1293 (1929); **36**, 57 (1930).

form satisfying the important antisymmetry requirement which includes the Pauli exclusion principle. Given a Ψ of this form, the effective potential assumption is partially, but definitely incompletely, relaxed by returning to the exact H and minimizing $E = \langle\Psi|H|\Psi\rangle$ by variation of the spatial parts of the spin orbitals $\chi_k = \phi_i\alpha$ or $\phi\beta$.

The two distinct aspects of the orbital approximation thus are the choice of form of the total wave function (a single determinant of orbitals) and the specific choice of orbitals (generally obtained by energy minimization). Since the electron density in a molecule is concentrated in regions around the nuclei, the usual approach is to expand molecular orbitals, ϕ, as linear combinations of atomic orbitals (LCAO expansion); the basis set is here a set of atomic orbitals. However, since there is no reason to assume that the optimum molecular orbital will be obtained using just the occupied orbitals of the constituent atoms as a basis, improvements are expected according to the hierarchy: (1) minimal basis (one basis function per atomic orbital); (2) extended basis (several basis functions per atomic orbital with angular momentum quantum numbers restricted to be the same as in atomic ground states); (3) extended basis plus polarization functions (inclusion of higher angular momentum basis functions or functions not centered on the nuclei).

The simplest extension (point 2) permits a variation in shape of atomic orbitals in the molecule and in different molecular orbitals, and (3) allows for polarizations at the molecular level which are not otherwise achievable, *e.g.*, d orbitals on C and p orbitals on hydrogen could be utilized. Applications using exponential (hydrogenic or Slater) or Gaussian basis functions can be classified accordingly, although in the latter it is common to regard fixed linear combinations of Gaussians as a single basis orbital (contracted or grouped Gaussians). Exponents or effective nuclear charges can be determined by calculations on atoms or, better, by optimization in the molecule; for large basis sets the latter is impractical, however, and the reliance is often on the size of the basis to accomplish changes in spatial shape. Basis function optimization does not obviate the inclusion of polarization functions in the basis since the latter play an essentially different role in representing the electron density.

Given a basis, $\{g_k\}$, and assuming all integrals over basis functions have been evaluated,[3] the optimization of molecular orbitals with respect to expansion coefficients, $\phi = \Sigma_k c_{ki} g_k$, can be accomplished using the SCF theory of Roothaan.[4] For the simplest case of doubly occupied spatial orbitals, the energy expression in terms of integrals over molecular orbitals is

$$E = \underbrace{\sum_i 2\langle\phi_i|h|\phi_i\rangle}_{\substack{\text{kinetic energy}\\ \text{and nuc-el}\\ \text{attraction}}} + \underbrace{\sum_i\sum_j 2\left(\phi_i(1)\phi_i(1)\left|\frac{1}{r_{12}}\right|\phi_j(2)\phi_j(2)\right)}_{\substack{\text{coulombic}\\ \text{repulsion, } J_{ij}}} - \underbrace{\left(\phi_i(1)\phi_j(1)\left|\frac{1}{r_{12}}\right|\phi_i(2)\phi_j(2)\right)}_{\substack{\text{exchange}\\ \text{interaction, } K_{ij}}}$$

Minimization with respect to c_{ki} gives the SCF matrix equation

$$[F_{kl} - \epsilon_i\delta_{kl}][C_i] = [0]$$

where in the above the molecular orbitals have been assumed to be orthonormal and the basis has been orthogonalized by construction, without loss of generality. The matrix elements, F_{kl}, of the secular equations involve the electron density which is not known until the problem is solved; thus the usual method of solution is an iterative one, carried out until the electron-repulsion field which defines F_{kl} is self-consistent.

A restatement of the problem, taking the solution $\{\phi_i\}$ as the basis $\{g_i\}$, gives zero for the off-diagonal matrix elements and diagonal elements which equal the Lagrangian multipliers

$$\epsilon_i = F_{ii} = \langle\varphi_i|h|\varphi_i\rangle + \sum_j(2J_{ij} - K_{ij})$$

Physically, ϵ_i is the energy associated with an electron in orbital ϕ_i since, if an electron were removed from ϕ_i to create a positive ion, and if all orbitals are *assumed* to be unchanged, then the total energy is changed by an amount ϵ_i, $-\epsilon_i = I_p$, ionization potential, from orbital ϕ_i, which is Koopmans' theorem. The theorem requires an assumption which is not realistic physically since all orbitals are expected to be different in the positive ion; its limited practical success is due to a partial cancellation of orbital optimization and correlation energy errors.

Once the orbital occupation is assumed, the orbital and total energy expressions can be deduced simply by counting the coulombic and exchange interactions, and this applies as well to open shell systems. But from the above definitions, it follows immediately that the total energy of the system is not equal to the sum of the orbital energies. Instead, for a closed-shell system, now including nuclear repulsion

$$E = \underbrace{\sum_i 2\epsilon_i}_{\substack{\text{sum of}\\ \text{orbital}\\ \text{energies}}} - \underbrace{\sum_{i,j}(2J_{ij} - K_{ij})}_{\substack{\text{electron}\\ \text{repulsion}\\ \text{energy}}} + \underbrace{V_N}_{\substack{\text{nuclear}\\ \text{repulsion}\\ \text{energy}}}$$

The latter two terms do not cancel even approximately, and thus it follows that orbital energies of many-electron SCF theory are not the same as those of an effective potential theory such as Hückel theory; equating orbital energies to ionization potentials is inconsistent with equating the sum of orbital energies to the total energy.

Obviously an infinite number of SCF solutions exist, one for each choice of basis. The only well-defined solution is that obtained when the basis is complete, *i.e.*, becomes infinitely flexible, which gives a definite total Ψ and total E, the Hartree–Fock solution. The remaining energy error is defined as the correlation energy of the system and as such is directly related to the incorrectness of the restrictive single-determinant of orbitals form for Ψ.[5] The prob-

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(3) A. C. Wahl, P. E. Cade, and C. C. J. Roothaan, *J. Chem. Phys.*, **41**, 2578 (1964) (Slater integrals), and earlier references contained therein; S. F. Boys, *Proc. Roy. Soc., Ser. A*, **200**, 542 (1950) (Gaussian integrals).

(4) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); **32**, 179 (1960); R. K. Nesbet, *Proc. Roy. Soc., Ser. A*, **230**, 312 (1955).

(5) P. O. Löwdin, *Advan. Chem. Phys.*, **2**, 207 (1959); *Phys. Rev.*, **97**, 1474 (1955).

Table I
Atomic Energies from Different Levels of *ab Initio* SCF Treatment[a]

Basis	Ground-state atomic energies, au H	C	O
Minimal Slater[b]	−0.5	−37.622	−74.540
Double-ζ Slater[b]	−0.5	−37.687	−74.804
Gaussian[c]	−0.4998	−37.685	−74.800
Hartree–Fock[b]	−0.5	−37.688	−74.809
Minimal Slater energy error	0.0[d]	1.8[d]	7.3[d]

[a] Variation in the accuracy of a given basis in different atoms can lead to pronounced effects in subsequent molecular applications; see changes in the minimal Slater energy error compared to Hartree–Fock for C and O. Total energies are in atomic units, 1 au = 27.21 eV. [b] Reference 7. [c] Reference 8. [d] Electron volts.

lem physically is that electrons cannot be treated independently in terms of an average electron-repulsion field; electron motions are correlated, tending away from a superposition in the same region of space.

The inclusion of correlation effects requires a more sophisticated form of Ψ than a single determinant, and possibilities include: the explicit introduction of interelectronic coordinates; valence bond constructions of Ψ and geminal or electron-pair formulations; or configuration interaction. The latter formulation, which utilizes a linear combination of determinants for the wave function, $\Psi = \Sigma_k C_k \Psi_k$, where the leading term is often an SCF solution, has thus far proved to be the simplest to implement computationally. Excited configurations, Ψ_k, are obtained by excitation from orbitals of the single determinant description to virtual or transformed virtual molecular orbitals of the SCF solution (conventional CI); alternatively, a limited number of different types of configurations can be assumed and the molecular orbitals optimized simultaneously in the multiconfigurational wave function (MCSCF procedure).[6]

Atomic Orbitals and Basis Functions

The solutions of the hydrogen atom, $\Psi_{nlm} = \exp(-a_n r)P(r,x,y,z)$, where P denotes a polynomial in the radial and cartesian coordinates r, x, y, and z, have guided the description of many-electron atoms; in the simplest sense a set of occupied orbitals with properly chosen exponents characterizes the atom. The optimum exponents can be determined by energy minimization and the conclusions can be understood as an approximate accounting for electron repulsion; the numerical choice of exponents is summarized approximately by Slater's rules.[2]

The problem is that the optimum orbitals for many-electron atoms in the single-determinant approximation are the Hartree–Fock orbitals, and these do not have precisely the same shape as hydrogenic or the closely related Slater orbitals; the differences are of great quantitative and sometimes qualitative importance. It has been shown, however, that sufficient flexibility is provided by taking linear combinations of exponential functions, or alternatively Gaussian functions, $\exp(-ar^2)$.[7,8] For both types of basis sets, as the atomic number increases, more components are required to achieve comparable closeness to the Hartree–Fock solution. The significance of this point can be seen even in atoms of the first row as shown in Table I; the energy error of the minimal Slater basis, $E_{1\text{-Slater}} - E_{\text{Hartree-Fock}}$, increases with the atomic number Z. Since much of this defect is concentrated in the valence shell, the values imply (although indirectly) that the effective electronegativity increase in going from carbon to oxygen is significantly less in the case of a single Slater basis than for the Hartree–Fock solution. The correlation energy error also increases with Z; for carbon the error is already quite large, 0.16 au = 4.4 eV, and clearly in a molecular problem errors of this magnitude are tolerable only if they can be regarded as mainly errors in the absolute energy, and less significantly errors in relative energies compared to the separated atoms.

In a molecular SCF treatment, it is anticipated that different choices of basis sets will yield results which differ in quantitative detail. The situation, however, is more serious than this, as can be illustrated by consideration of the water molecule in its equilibrium geometry. Two SCF solutions are considered, both using the simplest possible basis of seven orbitals, 1s, 2s, $2p_x$, $2p_y$, $2p_z$ oxygen atomic orbitals and 1s orbitals for each hydrogen in which the exponential scale factor is optimized.

In the first treatment, oxygen orbitals are chosen as the near-atomic Hartree–Fock atomic orbitals with no freedom allowed in the variation of component basis functions at the molecular level; in the second treatment, a single Slater function is used for each atomic orbital. The superiority of the first basis at the atomic level leads to a molecular energy ~7 eV lower than that of the second treatment. The dipole moment calculated from the first wave function is 2.5 D, compared to 1.85 D experimentally. The hydrogens are evidently too positive, and it follows that if the oxygen were more poorly described the dipole moment would decrease. It is noteworthy that this occurs as a natural consequence of the minimal Slater basis, for the reasons noted in the previous section, where the dipole moment is calculated as 1.95 D. Thus neither treatment is correct: the first basis is demonstrably imbalanced and the second is energetically defective.

A proper resolution of the problem is provided by a near-molecular Hartree–Fock treatment of H_2O by Neumann and Moskowitz.[9] Here the SCF treatment is performed using a flexible basis of s and p atomic orbitals plus d functions on oxygen and p functions on the hydrogens, giving a total energy of −76.059 au and μ = 1.995 D. Analysis shows that the d functions are essential in creating subtle changes in the electron density around oxygen and in the bonding region.

Studies of diatomic molecules and small polyatomic molecules provide the clearest indication of the sensitivity of molecular properties to the choice of basis and the reliability of the Hartree–Fock approximation itself. Table II shows typical data ob-

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(6) N. Sabelli and J. Hinze, *J. Chem. Phys.*, **50**, 684 (1969); G. Das and A. C. Wahl, *Phys. Rev. Lett.*, **24**, 440 (1970); A. C. Wahl and G. Das, *Advan. Quantum Chem.*, **5**, 261 (1970).

(7) E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962); E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963); E. Clementi, *ibid.*, **40**, 1944 (1964).

(8) H. Preuss, *Z. Naturforsch.*, **11**, 823 (1956); S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); J. L. Whitten, *ibid.*, **44**, 359 (1966).

(9) D. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **49**, 2056 (1968).

Table II
Comparison of Results of Different Levels of *ab Initio* Treatment of Several Small Molecules Showing the Sensitivity of Certain Properties to the Level of Treatment[a]

	D_e, eV	R_e, Å	ω_e, cm^{-1}	μ, D
CO				
Minimal Slater basis SCF[b]	6.20	*c*		0.464 C^-O^+
Double-ζ basis SCF[b]	5.74	*c*		0.393 C^+O^-
Hartree–Fock[b]	7.84	1.10	2431	0.274 C^+O^-
Hartree–Fock basis, CI[d]		*c*		0.077 C^-O^+
Experimental	11.24	1.13	2169	0.112 C^-O^+
F_2				
Hartree–Fock[e]	−1.3			
Hartree–Fock basis, MCSCF[f]	1.57	1.37	1021	
Experimental	1.65	1.42	892	
O_2				
Hartree–Fock[g]	1.43	1.152	2000	
Minimal basis, valence shell CI[g]	3.81	1.30	1582	
Extended basis, CI[g]	4.72	1.220	1614	
Experimental	5.21	1.207	1580	

	Inversion barrier, kcal	R_e, Å	θ, deg	μ, D
NH_3				
Minimal Slater basis SCF[h]	11.6	1.04	103	1.80
Double-ζ basis SCF[h]	−2.1	*c*	*c*	
Hartree–Fock[i]	5.1	1.00	107.2	1.66
	5.9	1.00	107	1.55
Experimental	5.8	1.01	106.7	1.48

[a] Small-basis SCF, Hartree–Fock, CI, and experimental results. [b] Reference 11. [c] Experimental value assumed. [d] Reference 29. [e] A. C. Wahl, *J. Chem. Phys.*, **41**, 2600 (1964). [f] Reference 6. [g] Reference 1. [h] Reference 10. [i] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970); R. M. Stevens, *ibid.*, **55**, 1725 (1971).

tained for several molecules. Equilibrium geometries are usually rather well predicted using a variety of basis sets; exceptions exist, however; for example, a double-ζ (s,p) basis SCF treatment of NH_3 yields a planar equilibrium geometry.[10] One-electron properties of the wave function such as the dipole moment show much greater sensitivity, sign changes of μ which is small in magnitude occur in CO when different basis sets are used, and in fact the near-molecular Hartree–Fock solution gives the wrong sign.[11] Dissociation energies are frequently too small owing to correlation errors associated with the formation of additional electron pairs in the molecule. When the proper dissociation of the molecule is to open shell species, the restricted Hartree–Fock wave function dissociates incorrectly to a mixture of atomic states as shown in Figure 1.

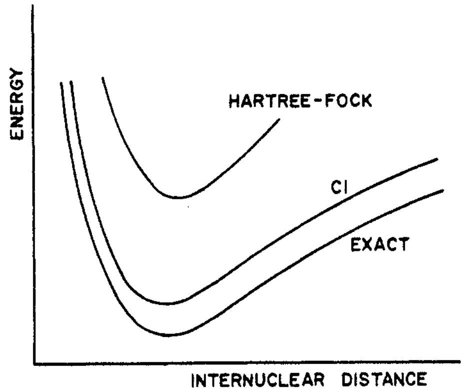

Figure 1. Typical diatomic molecule potential curve behavior when the dissociation is to open-shell atomic states. The incorrect dissociation of the restricted Hartree–Fock solution is corrected by inclusion of the proper configurations in the configuration interaction construction of the wave function.

Small basis set molecular treatments are on a more tenuous theoretical foundation. Generally the successful calculation of a series of molecules is required to achieve confidence that the basis is sufficiently well balanced to describe the energetics and molecular properties even approximately; see, for example, successful applications to calculations of geometries,[12] heats of reaction of closed-shell molecules,[13] rotational barriers,[14] and hydrogen bonding.[15]

Prediction of Wave Functions by Simple Bonding Arguments

If attempts are made to predict wave functions by qualitative reasoning along the lines of SCF theory, it is apparent that solutions quickly become inaccessible to prediction as the basis set is enlarged. It is possible, however, to predict the gross features of a single-determinant total wave function by simple arguments based on concepts of hybridization and bond orbital construction,[16-18] but by implementing these concepts quantitatively. An outline of the construction and a tabulation of results for the molecule H_2CO are given in Figure 2. Similar studies of other molecules have led to total energy errors within 0.015 au per atom excluding hydrogens compared to SCF solutions using the same basis, providing all hybridization and polarity parameters are optimized.[18] An important conclusion of these studies is that optimum hybrids generally are not directed along internuclear axes, and it turns out that the total energy is very sensitive to the hybridization. The latter is clearly a sufficient impediment to the prediction of simple wave functions of this type without energy calculations. Physically important delocalization effects not allowed in the construction likewise lead to energy discrepancies; in H_2CO, for example, it is found that abandoning the assumption of a completely localized lone-pair orbital on oxygen removes most of the energy discrepancy.

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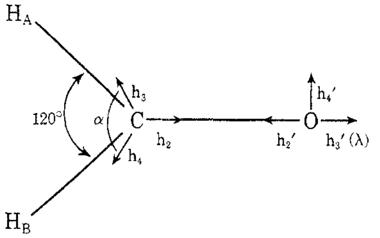
(10) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **45**, 888 (1966).
(11) W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965).
(12) L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969).
(13) L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, **91**, 2189 (1969); L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971).
(14) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963); L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).
(15) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971).
(16) J. E. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 1, 14 (1949); J. A. Pople, *ibid.*, **202**, 166 (1950).
(17) D. Peters, *J. Chem. Soc.*, 2015, 2003, 4017 (1963); *J. Chem. Phys.*, **46**, 4427 (1967).
(18) J. D. Petke and J. L. Whitten, *J. Chem. Phys.*, **51**, 3166 (1969).



h_1 C1s h_1' O1s

h_5 C2p$_\pi$ h_5' O2p$_\pi$

(hybrid parameters α, λ)

Bond orbitals and inner shell and lone-pair orbitals

$\phi_1 = h_1 = \text{C1s}$

$\phi_2 = h_1' = \text{O1s}$

$\phi_3 = h_4' = \text{O2p}$

$\phi_4 = h_2 + \gamma_\sigma h_2'$

$\phi_5 = h_5 + \gamma_\pi h_5' = \text{C2p}_\pi + \gamma_\pi \text{O2p}_\pi$

$\phi_6 = h_3 + \gamma_\sigma' \text{H}_\text{A}\text{1s}$

$\phi_7 = h_4 + \gamma_\sigma' \text{H}_\text{B}\text{1s}$

Bond polarity parameters: γ_σ, γ_π, γ_σ'

Symmetry orbitals: $\phi_6' = \phi_6 + \phi_7$, $\phi_7' = \phi_6 - \phi_7$

Total wave function

$\Psi = \det(\phi_1\phi_1\phi_2\phi_2 \ldots \phi_7'\phi_7')$

Results of Parameter Optimization and Comparison with SCF Solution

E, au	−113.6756	E(SCF)	−113.7035
μ, D	2.99	μ(SCF)	2.93 (2.33 expt)
ϕ, deg	128.5°		
γ_σ	1.51		
γ_σ'	0.58		
γ_π	1.10		

Figure 2. Hybridization, bond orbital construction of a total wave function for H_2CO using a minimal basis set. Parameters are determined by *ab initio* minimization of $\langle\Psi|H|\Psi\rangle$.[18]

It should be noted that the molecular orbitals predicted here may not correspond even remotely to the canonical SCF orbitals even though the total wave functions show close similarities energetically. This is because canonical SCF molecular orbitals are obtained by employing a side condition which reduces the off-diagonal Lagrangian multipliers to zero. Any linear transformation of the occupied molecular orbitals leaves the total ψ unchanged; thus

$$\psi = \det(\chi_1(1) \cdots \chi_N(N)) = \det[(\chi_1(1) \cdots \chi_N(N))SS^{-1}] = \det(S^{-1})\det(\chi_1'(1) \cdots \chi_N'(N))$$

where S is a matrix which transforms orbitals $\{\chi_k\}$ into $\{\chi_k'\}$. It follows that there exists an infinite number of orbitals which give the same total ψ which is the quantity of physical significance. It is for this reason that a choice of equivalent lone-pair orbitals on oxygen in H_2CO would lead to the same total ψ if all parameters are optimized; similar remarks apply to the choice of equivalent lone pair hybrids on O in H_2O. Such intermediate constructions may be useful in predicting parameters, but there is no physical significance associated with the different choices at the single determinant level for ψ; however, a specific choice of orbitals may facilitate construction of refinements of ψ or the analysis of subsequent processes, such as ionization or excitation where the canonical SCF orbitals are particularly useful.

Obviously, when hybrid and bond polarity parameters and the degree of localization become uncertain, the usefulness of the simple construction diminishes assuming that energy calculations are not to be performed. More important, however, is the fact that the entire argument is referenced to the simplest possible basis set. As noted above, molecular electron distributions involve important and sometimes subtle changes away from the simplest LCAO representation, and this is clearly the main point at which the qualitative reasoning breaks down. A localized representation of orbitals is still a valid and useful concept but, if the orbitals are to be determined directly, the procedure used must be capable of correcting errors due to prejudging the degree of localization incorrectly. Alternatively, a set of localized orbitals could be obtained by transformation of the SCF orbitals using, for example, the Edmiston and Ruedenberg criterion of orbital self-energy maximization.[19]

Orbital Energy Analysis

An analysis of orbital energies can provide immediate insight into the nature of bonding and the electron distribution. For example, a decrease or stabilization of a given ϵ_i on geometry variation can frequently be attributed to bonding or antibonding character or an increase in s character.[20] If an orbital, ϕ_i, such as an inner shell or lone-pair orbital, is invariant to a good approximation comparing one molecule with another, charge transfer into or from the spatial region proximate to ϕ_i is accompanied by a change in ϵ. Thus, from the expression $\epsilon_i = \langle\phi_i|h|\phi_i\rangle + \Sigma_j 2J_{ij} - K_{ij}$, electron transfer away from the region of ϕ decreases the electron repulsion field to give a more negative ϵ, *e.g.*, on F substitution in going from CH_4 to CH_3F, ϵ_{1s} of C decreases. The relationship of orbital energies to ionization potentials obtained by X-ray or photoelectron spectroscopy occurs *via* Koopmans' theorem, and since important orbital relaxations which occur in the ion are neglected in this argument, quantitative agreement should not be expected although trends can sometimes be rationalized. The absolute error in the case of oxygen 1s ionization, for example, is ~20 eV. Constrained SCF calculations on hole states of positive ions, however, have led to nearly quantitative agreement with measured ionization potentials.[21]

Inherent in orbital energy arguments in the absence of calculations is the assumption that certain SCF orbital(s) can be qualitatively identified and analyzed assuming the remaining orbitals in the molecule play a secondary role. The pyrazine molecule serves to illustrate problems in discussing energies of lone-pair orbitals and associated spectral predictions arising from n → π^* excitations. Figure 3 shows n_1 and n_2 hybrid orbitals which might be assumed to be localized on the two nitrogens of the molecule.

It might be argued that approximate SCF orbitals could be taken as the symmetry combinations $n_1 + n_2$ and $n_1 - n_2$ which would be expected to have nearly degenerate orbital energies in view of the spatial separation of n_1 and n_2. However, both semiem-

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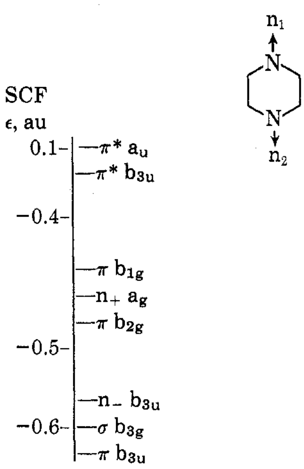
(19) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, S97 (1965).

(20) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(21) P. S. Bagus, *Phys. Rev. A*, **139**, 619 (1965).



Atomic populations	C	N	H
n_+	0.108	0.714	0.035
n_-	0.029	0.932	0.004

	Transition energies, eV	
State	CI	Exptl
$^1B_{2g}$ ($n_- \rightarrow \pi^*$)	5.65	
$^1B_{2u}$ ($\pi \rightarrow \pi^*$)	5.29	4.6–5.1
$^3B_{2g}$ ($n_- \rightarrow \pi^*$)	4.99	
$^1B_{3u}$($n_+ \rightarrow \pi^*$)	4.22	3.8–4.3
$^3B_{1u}$ ($\pi \rightarrow \pi^*$)	4.11	
$^3B_{3u}$ ($n_+ \rightarrow \pi^*$)	3.56	3.3–3.5

Figure 3. Pyrazine SCF orbital energies, Mulliken population analysis of orbitals n_+ and n_-, and vertical transition energies to low-lying excited states obtained by CI. A significant splitting, $\epsilon_{n+} - \epsilon_{n-} = 2.6$ eV, occurs in the ground-state SCF solution.[23]

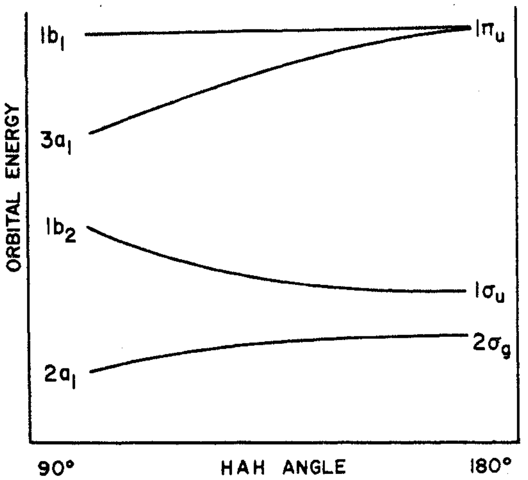


Figure 4. Orbital energy variations with angle HAH from *ab initio* calculations of BH_2^+ and BeH_2.[26] Except for the increase in ϵ_{2a1} with increasing HAH and elevation of the ϵ_{3a1} curve, the diagram is similar to the AH_2 correlation diagram of Walsh.[20]

pirical[22] and many-electron SCF solutions[23] show that this argument does not hold. The proper SCF orbitals are $\phi_1 = n_1 - n_2 + \lambda_1\sigma$ and $\phi_2 = n_1 + n_2 + \lambda_2\sigma$, where σ denotes ring σ orbitals; the antibonding combination, ϕ_1, is lowest in orbital energy (see Figure 3), with λ_1 small and $\epsilon_2 - \epsilon_1 = 2.6$ eV. The bonding combination is more delocalized ($\lambda_2 > \lambda_1$), the delocalization being a consequence of orthogonality to the ring σ system as opposed to a delocalization which leads to stabilization; alternatively, the ring σ system has been stabilized by borrowing lone-pair character. Such differences in lone-pair combinations persist in the excited states of pyrazine, giving a significant separation of $n_+ \rightarrow \pi^*$ and $n_- \rightarrow \pi^*$ states as shown in Figure 3. Similar remarks also apply to the lone-pair orbitals in the molecule glyoxal.

Orbital correlation diagrams introduced by Mulliken[24] and Walsh[20] and by Woodward and Hoffmann[25] have been extremely useful in making geometry, stereochemistry, and reactivity predictions. The Walsh diagrams for AH_2 systems are interesting to consider first because of an apparent inconsistency of the argument with SCF theory. The Walsh analysis of the orbital energy correlation diagram, ϵ *vs.* HAH angle θ, given in Figure 4, leads to different equilibrium geometry predictions depending on the number of electrons of A. The implication is that the sum of orbital energies, $\Sigma_i 2\epsilon_i$, qualitatively deduced, is related to the total energy of the system. As noted previously, SCF theory gives

$$E = \sum_i 2\epsilon_i - E_{\text{el-repl}} + E_{\text{nuc-repl}}$$

and the latter two terms do not cancel even approximately. There are two possibilities: either the orbital energies in the qualitative argument are not the same as in SCF theory even though they are generally identified with ionization potentials or there is an indirect explanation. A resolution of the latter premise is provided by the *ab initio* work of Peyerimhoff, *et al.*[26] Variation of E with θ gives

$$\frac{\partial E}{\partial \theta} = \frac{\partial \Sigma 2\epsilon_i}{\partial \theta} + \frac{\partial}{\partial \theta}(E_{\text{nuc-repl}} - E_{\text{el-repl}})$$

and the observation simply is that the derivative of the latter pair of terms is often small compared to $\partial\Sigma 2\epsilon_i/\partial\theta$; thus, the minima of E and $\Sigma 2\epsilon_i$ are approximately at the same value of θ. Further analysis reveals the point at which the argument fails. If the bonding is sufficiently ionic, the variation of $E_{\text{nuc-repl}} - E_{\text{el-repl}}$ with θ is not small and $\Sigma 2\epsilon_i$ does not show a minimum at the same value of θ as does E.

The dominance of certain molecular orbitals in determining molecular energy variations as a function of geometry has also been demonstrated by *ab initio* studies of the reaction of methylene molecules[27] and the conrotatory *vs.* disrotatory CH_2 rotations in the *cis*-butadiene → cyclobutene reaction,[28] in agreement with the Woodward-Hoffmann analysis.

Importance of Configuration Interaction

The assertion that single-determinant SCF theory (Hartree-Fock level) is adequate for determining ground-state molecular equilibrium geometries, properties, barriers, etc., is based on numerical experience as opposed to rigorous proof; exceptions do exist, and these can often be traced to physically significant effects which are not allowed in the single-determinant theory. Thus, for example, only when the Hartree-Fock Ψ_0 is known to dominate the CI expansion, $\Psi = C_0\Psi_0 + \Sigma_k C_k\Psi_k$, does Brillouin's theorem provide the rationale for prediction of one-electron properties at the Hartree-Fock level. For bond dissociation processes, and in the case of highly covalent bonds, the double occupancy of molecular orbitals inherent in the single-determinant representation forces unrealistic ratios of ionic to covalent character. This simple observation explains the incorrect dissociation of molecules to mixtures of

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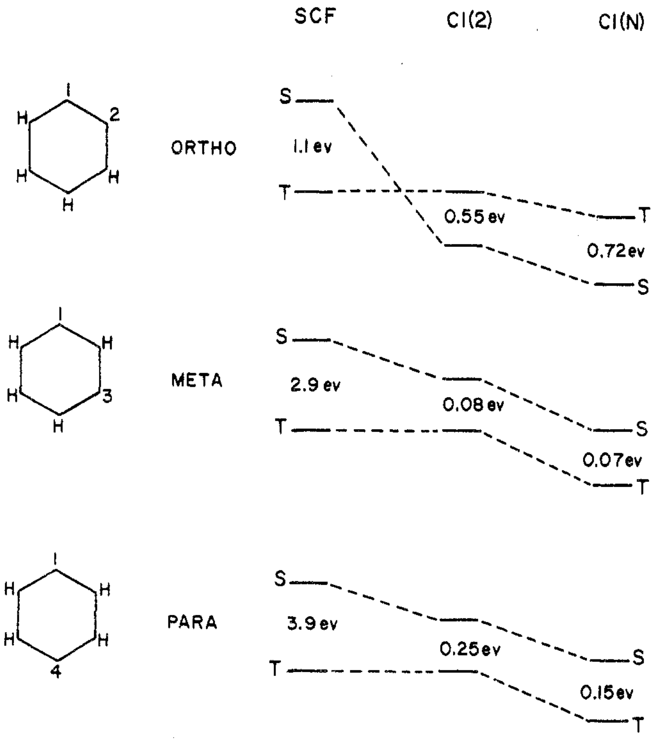

Figure 5. Changes in energy of the lowest singlet and triplet states of the benzynes due to configuration interaction, in the geometry of benzene.[30]

atomic or molecular fragment states when viewed at the Hartree–Fock level (see Figure 1). What is needed in the dissociation limit as well as in the equilibrium region is variability in ionic and covalent character, and this is the most elementary purpose of CI both in the simplest case of H_2 and in polyatomic molecules as well.

Other correlation effects involve additional angular and radial adjustments away from the superposition of electrons in the same region of space. Such effects are not well accounted for unless the basis is extended beyond the valence shell of the constituent atoms, regardless of the number of configurations in the CI expansion. Table II illustrates the improvement of dissociation energies, vibrational frequencies, and dipole moments due to CI, including a change of sign of the small dipole moment of CO.[29] Generally, however, in the case of molecular properties, it should not be expected that configuration interaction will overcome a deficiency in the orbital basis.

The benzyne molecule problem is a case in which the qualitative deficiency of single-determinant SCF description can be spotted by elementary considerations. The molecule, shown in Figure 5, is treated as having the geometry of benzene, and both singlet and triplet possibilities for the ground state are considered;[30] relaxation of the geometry by shortening the C_1C_2 bond would favor the singlet state. Single-determinant SCF calculations show the triplet state of benzyne to be significantly lower in energy by 1.14 eV. However, a simple two-configuration CI reverses the order, and further CI involving more extensive excitations results in a generally parallel lowering of both states. The interpretation is simple, the same as used to describe the bonding in H_2; the third bond of benzyne is sufficiently weak so as to require a greater ratio of covalent to ionic character which cannot be achieved in the single-determinant SCF representation.

Excited Electronic States

CI studies of excited states have now been reported for a variety of diatomic and polyatomic molecules, and it is possible to conclude that CI applications of only moderate complexity are often quite satisfactory for the description of $^{1,3}(n \rightarrow \pi^*)$, $^{3}(\pi \rightarrow \pi^*)$, and certain Rydberg states.[31-37] Difficulties are encountered in the description of some, but not all, $^{1}(\pi \rightarrow \pi^*)$ states which are thought to be responsible for the most intense absorptions observed experimentally. Calculated transition energies are sometimes several electron volts too high when simple basis sets are employed.[31,32] Correction of the difficulty has been found possible by two different types of treatment: (1) an inclusion of spatially diffuse orbitals in the basis set which gives rise to $^{1}(\pi \rightarrow \pi^*)$ states which qualitatively resemble Rydberg (spatially diffuse) states;[33-35] or (2) a more complex level of CI treatment involving extensive $\sigma \rightarrow \sigma^*$ excitation and refinements in the treatment of ionic-like charge distributions which occur in the π system of $^{1}(\pi \rightarrow \pi^*)$ states.[31,36,37] At the present time it is not clearly understood quantitatively the extent to which these different effects occur simultaneously. However, neither resolution of the $^{1}(\pi \rightarrow \pi^*)$ problem is in agreement with the widely accepted view that the excited state can be viewed simply as an excitation from a ground state occupied orbital to an unoccupied valence shell molecular orbital.

A few general remarks are now made about the organization of a CI treatment of excited states starting with a known SCF description of the ground state. The virtual orbitals are determined by an electron-repulsion field corresponding to orbitals occupied in the ground state and therefore correspond roughly to orbitals of the negative ion. Thus, there is little reason to expect that these orbitals should be appropriate for an excited state. What is needed to obtain an initial description of an excited state is at least optimization of the orbital to which excitation occurs.[31,38]

Virtual orbitals which are most appropriate for the inclusion of correlation corrections at the CI level are not however obtained in principle by the same type of transformation which yields the initial description; the former orbitals are more closely related to optimizing the interaction of double excitation con-

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figurations with the simplest determinantal wave function. If, however, all orbitals are retained for use in generating excited configurations, the transformation step is of no consequence theoretically, and approximations to this limit have been explored in the iterative natural orbital method of constructing CI wave functions.[35] Another alternative is the MCSCF approach in which a relatively small number of different types of configurations is selected, followed by optimization of all important molecular orbitals.

Some complexities which emerge as important in the description of excited states, particularly in certain $^1(\pi \rightarrow \pi^*)$ states, are worth examining in order to understand potential deficiencies of *ab initio* CI treatments at their present stage of development.[31,33,37] The π system of ethylene is considered as an example, initially using a minimal basis of p_π orbitals on each carbon, labeled A and B. The π and π^* orbitals are completely determined by symmetry: $\pi^* = \mathrm{A} - \mathrm{B}$ and $\pi = \mathrm{A} + \mathrm{B}$ (unnormalized). Three states are of interest, the ground state $^1\psi_\mathrm{G}$, the triplet excited state $^3\psi_\mathrm{E}$, and the singlet excited state $^1\psi_\mathrm{E}$,

$$^1\psi_\mathrm{E} = [\mathcal{A}(\pi(1)\bar{\pi}^*(2)) - \mathcal{A}(\bar{\pi}(1)\pi^*(2))]2^{-1/2} = [A(1)A(2) - B(1)B(2)][\mathrm{spin}]$$

$$^3\psi_\mathrm{E} = \mathcal{A}(\pi(1)\pi^*(2)) = [A(1)B(2) - B(1)A(2)][\mathrm{spin}]$$

$$^1\psi_\mathrm{G} = \mathcal{A}(\pi(1)\bar{\pi}(2)) = [A(1)A(2) + B(1)B(2) + A(1)B(2) + B(1)A(2)][\mathrm{spin}]$$

in which the notation surpresses the doubly occupied σ orbitals. Qualitative differences in the nature of these states are evident from expansions of the determinants showing the component electron distributions.

Even if the basis is expanded and multiconfigurational descriptions of the states are allowed, it is easily proved by finding the natural orbitals of the two-electron systems that the above descriptions are the principal components of the states although the orbitals A and B are no longer simple atomic orbitals nor are they the same in different states. The first point is that the $^1(\pi \rightarrow \pi^*)$ and $^3(\pi \rightarrow \pi^*)$ states are very different in character, the former being entirely ionic and the latter covalent. Apropos semiempirical parameters, this means that different choices may well be required for singlet and triplet states even though they arise from the same molecular orbital excitation, $\pi \rightarrow \pi^*$.

As for CI refinements of these descriptions, it is evident that the correlation effects are different in the three states; a simple CI treatment using a restrictive atomic orbital basis may be capable only of varying ratios of ionic to covalent character, and this significantly improves only the ground state. In order to alleviate the electron repulsion in the ionic distribution of $^1\psi_\mathrm{E}$, expansion of the spatial extent of A and B may be required tending toward a Rydberg description. Angular correlations in the doubly occupied $p\pi$ orbitals of $^1\psi_\mathrm{E}$ may be extremely important, as well as orbital polarization; both of these effects require proper d orbitals in the basis and such functions frequently are not present in treatments of large molecules. It is also easy to see a physical significance of $\sigma \rightarrow \sigma^*$ excitations, apart from their role in adjusting the ionic and covalent character of σ bonds. If $^1\psi_\mathrm{E}$ is written as $^1\psi_\mathrm{E} = \psi_\mathrm{E}{}^\mathrm{I} - \psi_\mathrm{E}{}^\mathrm{II}$ and the question asked how can the ionic components I and II be stabilized individually, the conclusion evidently is that the σ system of I should be polarized toward II and that of II toward I. Taking the components simultaneously shows that the σ polarization effects cancel only partially in higher order, thus leaving a specific interorbital σ–π correlation effect.

In principle, if the basis is adequate, all of the above CI effects can be treated purely numerically; the difficulty in practice is that in most polyatomic molecules there are limitations on the capability of the basis and the CI expansion itself may be too restrictive. All of the above modes for relaxing unfavorable electron distributions, of course, occur simultaneously, and the problem is that if certain modes are not allowed due to practical restrictions, the energy variational nature of the CI calculation causes the modes which are allowed to be accentuated, and this can lead to erroneous conclusions physically about the nature of excited states.

Concluding Remarks

In each of the variety of calculations described here as *ab initio,* there exist constraints imposed to achieve either tractability or simplicity and these in turn can have important physical consequences. The understanding of precisely how specific constraints affect a prediction is an evolving proposition, as also is the average level of sophistication of reported *ab initio* treatments. At the present time, some of the underlying uncertainties are definitely known and these can often be understood in terms of a few examples and counterexamples, some of which have been discussed here. The availability of quantitative information from *ab initio* studies should serve another important purpose, that of delineating the role of certain concepts in qualitative and semiempirical descriptions of bonding.