Wave Functions for Small Molecules based on Linear Combinations of Atomic Orbitals

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1 Atomic Orbitals in Molecular Wave Functions

That molecules are made up of atoms is not in itself a good reason for constructing molecular wave functions from atomic wave functions. The LCAO (linear combinations of atomic orbitals) procedure has no fundamental wave-mechanical basis, and it can thus be justified in a quantitative sense only by the evidence of a large number of uniformly successful calculations on a variety of molecules. It is only very recently that this evidence has become available. Because of the difficulty caused by the number and the complexity of the electron-repulsion integrals for all but the smallest molecules, the accumulation of the required information has had to await the development of large-scale electronic computing techniques.

Until the late nineteen-fifties most LCAO calculations were restricted to two widely different groups of molecules: on the one hand there were strict and accurate calculations on a few exceedingly small molecules, and on the other there were Hückel (or modified Hückel) calculations on a great number of large π-orbital systems. The former were too unrepresentative to be generally informative, the latter too heavily loaded with experimental data.

It is obvious from the Bibliography in Section 6 that great progress has been made during the last decade in bridging the gap between the two groups of molecules. It is now known not only that LCAO calculations can give molecular energies correct to within *ca.* 0·5%, but that reasonable estimates can be made of spectroscopic constants and various molecular properties dependent on electronic charge distribution. Computations on strict wave-mechanical principles have been carried out on molecules having nearly seventy electrons, without recourse to experimental data.

The work is constantly being extended, but the main conclusions are now clear, so this seems an appropriate time to review the subject for chemists in general, and to indicate both what has been achieved and what has not. Several earlier accounts have been given for specialist readers, the latest and most comprehensive being by Krauss.[1]

An admirably clear summary of the position in 1959 was provided by Allen and Karo,[2] and we take this as our starting point.

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[1] M. Krauss, 'Compendium of *Ab Initio* Calculations of Molecular Energies and Properties', Technical Note 438, National Bureau of Standards, Washington, 1967.
[2] L. C. Allen and A. M. Karo, *Rev. Mod. Phys.*, 1960, **32**, 275.

2 Molecular-orbital Wave Functions

If, as in the majority of cases considered in this Review, N molecular orbitals $\chi_1, \chi_2, \ldots, \chi_N$, are used to describe the ground state of a $2N$-electron molecule, there is only one way of distributing the spin factors α and β, and the complete wave function is thus the single determinant[3]

$$\Psi = \begin{vmatrix} \chi_1(1) & \chi_1(2) & \chi_1(3) & \chi_1(4) & \ldots & \chi_1(N-1) & \chi_1(N) \\ \bar{\chi}_1(1) & \bar{\chi}_1(2) & \bar{\chi}_1(3) & \bar{\chi}_1(4) & \ldots & \bar{\chi}_1(N-1) & \bar{\chi}_1(N) \\ \chi_2(1) & \chi_2(2) & \chi_2(3) & \chi_2(4) & \ldots & \chi_2(N-1) & \chi_2(N) \\ \bar{\chi}_2(1) & \bar{\chi}_2(2) & \bar{\chi}_2(3) & \bar{\chi}_2(4) & \ldots & \bar{\chi}_2(N-1) & \bar{\chi}_2(N) \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \chi_N(1) & \chi_N(2) & \chi_N(3) & \chi_N(4) & \ldots & \chi_N(N-1) & \chi_N(N) \\ \bar{\chi}_N(1) & \bar{\chi}_N(2) & \bar{\chi}_N(3) & \bar{\chi}_N(4) & \ldots & \bar{\chi}_N(N-1) & \bar{\chi}_N(N) \end{vmatrix} \tag{1}$$

where χ_i signifies $\chi_i\alpha$ and $\bar{\chi}_i$ signifies $\chi_i\beta$. The determinant (1) is obtained by imposing the Pauli antisymmetry requirement on the much simpler Schrödinger function:

$$\chi_1(1)\,\bar{\chi}_1(2)\,\chi_2(3)\,\bar{\chi}_2(4)\ldots\chi_N(N-1)\,\bar{\chi}_N(N) \tag{2}$$

Because it is formulated by ignoring electron-repulsion terms in the Hamiltonian operator, the simple product (2) cannot be an exact solution of the relevant Schrödinger energy equation, however accurate the individual molecular orbitals may be; the same is true of the determinant (1). If all the molecular orbitals have their best possible forms (and not merely the best forms obtainable by varying a small number of parameters such as LCAO coefficients or orbital exponents), the wave function (1) is described as a Hartree–Fock or self-consistent-field wave function. The difference between the Hartree–Fock energy for an atom or molecule and the energy obtained from an exact wave function with the same Hamiltonian operator is known (conveniently, but for reasons which transcend the basic postulates of wave mechanics) as the correlation energy. The correlation energy of a molecule is almost always larger than the sum of the correlation energies of the component atoms.[4]

The wave functions discussed in this Review, though very often (and very improperly) described as Hartree–Fock or self-consistent-field wave functions, are in fact just LCAO wave functions in which each molecular orbital χ is written as a linear combination of atomic orbitals $\psi_a, \psi_b, \ldots, \psi_m$:

$$\chi = c_a\psi_a + c_b\psi_b + \ldots + c_m\psi_m \tag{3}$$

The m atomic orbitals in any calculation are known as the basis set. The greater the value of m, the more nearly an LCAO wave function approaches the Hartree–Fock wave function.

The atomic orbitals are assigned the usual spherical polar form[3] $\psi = R\Theta\Phi$, where the angular factors Θ and Φ are exactly the same as for the hydrogen atom, and R is given by:

$$R = r^{n-1}\,e^{-\zeta r} \tag{4}$$

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[3] C. A. Coulson and E. T. Stewart, in 'The Chemistry of Alkenes', ed. S. Patai, Interscience, New York, 1964, ch. 1.

[4] R. K. Nesbet, *Adv. Chem. Phys.*, 1965, **9**, 321.

(as in a Slater[5] orbital). For each atom in each molecule the 'orbital exponent' ζ depends not only on the quantum numbers n and l, but also (because molecules lack the characteristic spherical symmetry of atoms) on the quantum number m.

Optimising the molecular wave functions subject to the restrictions imposed by the forms (3) and (4) requires the minimisation of the electronic energy with respect to the coefficients c in the molecular orbitals (3) and the exponential parameters ζ in the atomic orbitals (4). The variation of the coefficients is straightforward in principle,[6] and is normally effected by a method of successive approximation devised by Roothaan;[7] the variation process is always carried to completion. On the other hand, optimisation with respect to all the atomic-orbital exponential parameters ζ in a molecular-orbital wave function is a very tedious process which can only be carried out by trial and error; it is usually left incomplete or omitted altogether.

The values of ζ used in a molecular-orbital wave function are often those appropriate to variational calculations on the free atoms, or simply those specified by Slater's Rules.[5] As a half measure, the members of a set of arbitrarily chosen orbital exponents may all be multiplied by the same scale factor. If the energy is minimised with respect to the scale factor, the variation principle and the virial theorem can be satisfied simultaneously.[8]

As far as computation is concerned, an LCAO wave function can usually be improved more efficiently by extending the basis set than by optimising the atomic orbital exponents. The larger the basis set, the less the improvement that remains to be brought about by varying the atomic-orbital exponents. Of course the 'chemical' interpretation of a wave function is simplest when the basis set is as small as possible.

A method of extending the basis set which is directly related to the choice of orbital exponents involves the use of Clementi's 'double-zeta' atomic orbitals,[9] in which the simple exponential factor $\exp(-\zeta r)$ in the radial function (4) is replaced by a linear combination of two exponential factors, $\exp(-\zeta_1 r)$ and $\exp(-\zeta_2 r)$. Optimum values of ζ_1 and ζ_2 are known for atomic orbitals with $Z \leqslant 36$. These same exponents are used in a molecular calculation, but the linear-combination coefficients are included in the variation process applied to the coefficients in equation (3).

If a molecular wave function based on a single configuration of molecular orbitals is insufficiently accurate for its purpose, the spin–orbital product (2) must be replaced by a linear combination of spin–orbitals products, *i.e.* the determinant (1) must be replaced by a linear combination of determinants:

$$\Psi = C_1\Psi_1 + C_2\Psi_2 + \ldots \qquad (5)$$

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[5] J. C. Slater, 'Quantum Theory of Atomic Structure', McGraw-Hill, New York, vol. 1, 1960.

[6] J. C. Slater, 'Electronic Structure of Molecules', McGraw-Hill, New York, 1963; W. N. Lipscomb, *Adv. Magn. Resonance*, 1966, **2**, 137.

[7] C. C. J. Roothaan, *Rev. Mod. Phys.*, (*a*) 1951, **23**, 69; (*b*) 1960, **32**, 179.

[8] P.-O. Löwdin, *J. Mol. Spectroscopy*, 1959, **3**, 46; A. D. McLean, *J. Chem. Phys.*, 1964, **40**, 2774.

[9] E. Clementi, *J. Chem. Phys.*, 1964, **40**, 1944; E. Clementi, R. Matcha, and A. Veillard, *ibid.*, 1967, **47**, 1865.

Each spin–orbital product or determinant represents one configuration. Variational techniques for determining the coefficients C_1, C_2, . . . have been described by Clementi.[10] The purely mathematical process of building up a wave function by linear combination of single-configuration determinants is known (misleadingly, but almost universally) as configuration 'interaction'.

Even a single-configuration wave function may have the form (5) if there are several equivalent ways of assigning spin factors to the molecular orbitals, each determinant corresponding to one assignment. This will be the case if (as in most excited states) there are unpaired molecular orbitals.[3] In these circumstances the linear-combination coefficients are found by using the Schrödinger spin operators; the variation principle is not required for determining the coefficients C_1, C_2, . . . in (5), but the form of (5) complicates the algebraic procedures[7b] used in determining the coefficients c_a, c_b, . . . in (3).

3 Types of Basis Function

Although this Review is concerned with the construction of molecular orbitals from atomic orbitals, we must mention, in passing, other types of basis function which are at present of considerable importance.

Even with the extensive computing resources now available, the accurate evaluation of the three- and four-centre integrals which arise in LCAO calculations on polyatomic molecules still takes a considerable time. These are electron-repulsion integrals in which the four atomic orbitals in the integrands are functions of co-ordinates having three or four different origins (at the various nuclei). The difficulty is greatest for non-linear molecules, which accounts for the otherwise surprising number of unusual linear molecules listed in Section 6.

The evaluation of individual three- or four-centre integrals can be greatly simplified by replacing atomic orbitals of the Slater type (4) by Gaussian functions,[11,12] in which the exponents are $-\zeta r^2$ instead of $-\zeta r$. Unfortunately, to obtain wave functions of comparable accuracy requires about five times as many Gaussian functions as Slater functions; *i.e. ca.* 5^4 ($= 625$) times as many integrals have to be evaluated. Nevertheless Gaussian basis sets have been used with considerable success for quite large molecules (*e.g.* formyl fluoride,[13] benzene,[14] pyridine,[15] naphthalene[16]), and even to calculate energy surfaces for the NH_3–HCl reaction.[17]

'Gaussian lobe' functions utilise the relative ease of evaluating multicentre integrals in another way. In this method (Allen[12]) angularly dependent atomic

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[10] E. Clementi, *J. Chem. Phys.*, 1967, **46**, 3842; A. Veillard and E. Clementi, *Theor. Chim. Acta*, 1967, **7**, 133.

[11] I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta*, 1966, **6**, 191.

[12] L. C. Allen, *Internat. J. Quantum Chem.*, 1967, **1**, S39.

[13] I. G. Csizmadia, M. C. Harrison, and B. T. Sutcliffe, *Theor. Chim. Acta*, 1966, **6**, 217.

[14] J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, 1965, **43**, 3287.

[15] E. Clementi, *J. Chem. Phys.*, 1967, **46**, 4731.

[16] R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Letters*, 1969, **3**, 37.

[17] E. Clementi, *J. Chem. Phys.*, 1967, **46**, 3851; 1967, **47**, 2323; E. Clementi and J. N. Gayles, *ibid.*, 1967, **47**, 3837.

orbitals are simulated by suitable positioning of groups of Gaussian 'lobes' (purely radial Gaussian functions).

The problem of evaluating multicentre integrals can be avoided altogether by the use of single-centre basis sets.[18] For example, a wave function for hydrogen fluoride[19] can be constructed from F orbitals only, and a wave function for methane[20] from C orbitals only. In a similar way, a wave function for acetylene[21] can be constructed from orbitals centred on the two C atoms. As would be expected, single-centre calculations require very large basis sets, and they are of limited application.

As procedures for the evaluation of multicentre integrals are continuing to improve,[22] it seems likely that atomic orbitals will eventually displace Gaussian functions from routine molecular calculations. The recent publication by Stevenson and Lipscomb[23] of LCAO wave functions for ScH_3NH_3 and TiH_3F is a notable step in this direction.

4 Carbon Monoxide

In this Section we illustrate the information that may be obtained from LCAO calculations by reference to carbon monoxide, one of the molecules which have been studied most intensively.

A. Wave Functions.—The CO molecule has fourteen electrons, so at least seven atomic orbitals must be combined to construct the seven molecular orbitals (or fourteen molecular spin-orbitals) required for the simplest type of ground-state wave function. The seven atomic orbitals must obviously include $1s, 2s, 2p_z$ $(=2p\sigma)$ from each atom. It is impossible to choose any other $2p$ orbital without being committed to both $2p_x$ and $2p_y$ (which are degenerate) from each atom; so a minimum basis set comprises ten atomic orbitals. These give ten linearly independent molecular orbitals instead of the seven required for a wavefunction of type (1). The three molecular orbitals which are superfluous in the ground state ('virtual' orbitals) can be used in excited states;[7a] but strictly a separate minimisation of all atomic-orbital coefficients should be carried out for each excited state.[7b]

As shown in Section 6, minimum-basis-set calculations have been performed by Ransil,[24] using atomic-orbital exponents determined both by Slater's Rules and by atomic variational calculations, and by Sahni *et al.*[25] and Huo,[26] using atomic-orbital exponents varied in the molecular calculation. Nesbet,[27] Huo,[26] and

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[18] B. D. Joshi, *J. Chem. Phys.*, 1967, **46**, 875.
[19] R. Moccia, *J. Chem. Phys.*, 1964, **40**, 2164.
[20] D. M. Bishop, *Mol. Phys.*, 1963, **6**, 305.
[21] J. R. Hoyland, *J. Chem. Phys.*, 1968, **48**, 5736.
[22] R. E. Christoffersen and K. Ruedenberg, *J. Chem. Phys.*, 1968, **49**, 4285; L. S. Salmon, F. W. Birss, and K. Ruedenberg, *ibid.*, 1968, **49**, 4293; D. M. Silver and K. Ruedenberg, *ibid.*, 1968, **49**, 4301, 4306 (and references cited therein).
[23] P. E. Stevenson and W. N. Lipscomb, *J. Chem. Phys.*, 1969, **50**, 3306.
[24] B. J. Ransil, *Rev. Mod. Phys.*, 1960, **32**, 239, 245.
[25] R. C. Sahni, C D. La Budde, and B. C. Sawhney, *Trans. Faraday Soc.*, 1966, **62**, 1933.
[26] W. M. Huo, *J. Chem. Phys.*, 1965, **43**, 624.
[27] R. K. Nesbet, *J. Chem. Phys.*, 1964, **40**, 3619.

Yoshimine and McLean[28] have carried out calculations with a variety of extended basis sets. Extension of the basis set has been found (as is generally the case) to be more effective than optimising orbital exponents[26] or using configuration interaction with a small basis set. With a minimum basis set, a single-determinant function of type (1) gives 99·09 % of the observed molecular energy, and a 14-term function of type (5) gives only 0·04 % more.[29] Single-determinant extended-basis-set calculations give *ca.* 99·5 %.

The molecular orbitals comprising Ransil's[24] wave function are reproduced in Table 1. They are of three symmetry types, σ, π_x, and π_y. It is obvious that the 1σ and 2σ molecular orbitals are virtually unchanged atomic orbitals: $1\sigma \approx 1s_{\text{O}}$ and $2\sigma \approx 1s_{\text{C}}$. This is because the two $1s$ orbitals are concentrated so much about their respective nuclei that they do not overlap appreciably either with each other or with the other atomic orbitals in the system. This is clear also from the orbital energies: the 1σ and 2σ molecular orbital energies are not significantly different from the corresponding orbital energies in other molecules containing the same atoms, or indeed from the $1s$ orbital energies in the free atoms.

It will be noted that there is no lack of combination between $2s$ and $2p_z$ orbitals in all the higher-energy σ orbitals; hybridisation is a feature of all properly optimised LCAO wave functions, and is not restricted to particular electronic or geometrical configurations. The sharp quantum distinction between s and $p\sigma$ orbitals, which depends upon the spherical symmetry of atoms, is lost in molecules. The ratio between $2s$ and $2p_z$ coefficients in Table 1 varies from one orbital to another; the fixed ratio which is found in simple valence-bond functions is not determined variationally, and has no relevance in molecular-orbital wave functions.

Wave functions similar to that in Table 1 have been discussed by Coulson and Stewart[3] in more detail than can be given here.

B. Dissociation Energy.—Because the correlation energy of a molecule almost always exceeds the sum of the correlation energies of its atoms, Hartree–Fock calculations tend to underestimate dissociation energies, sometimes very grossly. The same is usually true of single-configuration LCAO approximations to Hartree–Fock calculations, as is shown for CO in Table 2. It happens in the results quoted that the better wave function gives the better dissociation energy, but this is not a general feature. Extending a basis set may either increase or decrease a calculated dissociation energy, depending on whether the improvement in the molecular energy is greater or less than the improvement in the sum of the atomic energies.

It is very well known[3] that one of the principal disadvantages of molecular-orbital wave functions is that they correspond to charged, instead of neutral, atomic dissociation products. It is possible to estimate the correlation energy of a molecule by assuming it to be approximately the same as that of the Hartree–

[28] M. Yoshimine and A. D. McLean, *Internat. J. Quantum Chem.*, 1967, **1**, S313.
[29] S. Fraga and B. J. Ransil, *J. Chem. Phys.*, 1962, **36**, 1127.

Table 1 *Molecular-orbital wave function for the ground state of carbon monoxide*[a]

Configuration:* $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi_x{}^2 1\pi_y{}^2 5\sigma^2$ Internuclear distance = 2·132 B† = 1·1282 Å

*Molecular Orbital**	*Coefficients of carbon orbitals*‡					*Coefficients of oxygen orbitals*‡					*Orbital energy*§
	1*s*	2*s*	$2p_z$¶	$2p_x$	$2p_y$	1*s*	2*s*	$2p_z$¶	$2p_x$	$2p_y$	(H†)
1σ	− 0·0002	0·0069	0·0063			− 0·9960	− 0·0202	− 0·0058			− 20·706
2σ	0·9964	0·0171	0·0059			− 0·0002	− 0·0054	− 0·0007			− 11.353
3σ	− 0·1152	0·2401	0·1687			− 0·2148	0·7588	0·2232			− 1·499
4σ	0·1468	− 0·5383	− 0·0668			0·1263	0·6529	− 0·6350			− 0·732
5σ	− 0·1403	0·7579	− 0·5658			0·0022	0·0366	− 0·4379			− 0·481
6σ	− 0·0916	0·9694	1·2509			0·1197	− 1·1289	− 0·9415			0·932
$1\pi_x$				0·4686					0·7712		− 0·583
$1\pi_y$					0·4686					0·7712	− 0·583
$2\pi_x$				0·9225					− 0·6897		0·261
$2\pi_y$					0·9225					− 0·6897	0·261

Molecular energy: — 112·344 H (calculated); — 113·377 H (observed).

[a] Ref. 24.

* The numerals preceding the symbols σ and π are not quantum numbers but merely serial numbers indicating the order of orbital energies for each symmetry type. The molecular orbitals 6σ, $2\pi_x$, and $2\pi_y$ ('virtual orbitals') are not relevant in the ground state.

† 1 B (= Bohr) = 0·052917 nm; 1 H (= Hartree) = 4·3594 aJ (atomic units for infinite nuclear mass).

‡ Atomic-orbital exponents as specified by Slater's Rules.

¶ The positive z axes point from the nuclei towards each other.

§ The orbital energy ϵ associated with a particular spin-orbital consists of (i) the kinetic energy of the spin-orbital, (ii) the potential energy of attraction between the spin-orbital and all the nuclei, (iii) the potential energy of repulsion between the spin-orbital and all the other spin-orbitals in the system. For a formal definition see refs. 3 and 6.

Fock ionic dissociation products.[30] As the correlation energies of atoms and ions with $Z \leqslant 30$ are known,[31] this provides a means of improving calculated molecular energies, and hence calculated dissociation energies.[32] Nesbet[27] has estimated the correlation energy of $C^{2+} + O^{2-}$ to be 3·18 ev higher than that of C + O. If a correction of this amount is added to the better of the two calculated dissociation energies (7·84 ev) quoted in Table 2, the adjusted value (11·02 ev) very closely approaches the observed dissociation energy (11·24 ev).

Other methods of adjustment have been suggested.[33,34]

Table 2 *Molecular properties of the ground state of carbon monoxide*

	Calculated with minimum basis set	*Calculated with extended basis set*[d]	*Observed*[e]
Molecular energy (H)	– 112·344[a]	– 112·786	– 113·377
Error in calculated molecular energy (%)	0·91	0·52	
Dissociation energy (ev)	5·38[a]	7·84	11·242
Internuclear distance at energy minimum (B)	2·182[b]	2·081	2·132
Spectroscopic constants:			
ω_e (cm^{-1})	2398·4[b]	2431	2169·8
$\omega_e x_e$ (cm^{-1})	8·989[b]	11·69	13·295
B_e (cm^{-1})	1·8419[b]	2·027	1·9313
α_e (cm^{-1})	0·0113[b]	0·01525	0·0175
k (10^5 dyne cm^2)		23·86	19·02
Dipole moment (D)	– 0·730[a]	0·274	– 0·118
Quadrupole coupling constant (10^{-24} cm^2)		– 0·0214	0·0163
Electric field gradient at oxygen nucleus (atomic units)	– 0·15[c]	– 0·679	– 0.64

[a] Ref. 24; [b] Ref. 25; [c] Ref. 49(*a*); [d] Ref. 26; [e] Quoted in ref. 26.

C. Spectroscopic Constants.—By performing an LCAO calculation for a range of internuclear distances, it is possible to express the molecular energy as a function of internuclear distance, and so to calculate spectroscopic constants. Table 2 shows that the results are by no means perfect, as would be expected if only

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[30] R. K. Nesbet, *J. Chem. Phys.*, 1962, **36**, 1518.

[31] E. Clementi and A. Veillard, *J. Chem. Phys.*, 1966, **44**, 3050.

[32] E. Clementi, *J. Chem. Phys.*, 1963, **38**, 2780; 1963, **39**, 487.

[33] K. Carlson and P. Skancke, *J. Chem. Phys.*, 1964, **40**, 613; V. McKoy, *ibid.*, 1965, **42**, 2232; F. Grimaldi, *ibid.*, 1965, **43**, S59.

[34] C. Hollister and O. Sinanoglu, *J. Amer. Chem. Soc.*, 1966, **88**, 13.

because of the faulty estimation of dissociation energy. McLean[35] and Schwendeman[36] have discussed the various sources of error.

A more subtle, though not necessarily more accurate, method of calculating spectroscopic constants involves the use of the Hellmann–Feynman theorem[37] (which applies to genuine Hartree–Fock wave functions[38] as well as to exact wave functions).

D. Electronic Charge Distribution.—There is good reason to believe that the electronic charge distribution corresponding to a Hartree–Fock wave function should not differ significantly from the true distribution.[39,40] It may be hoped that the same is true of an LCAO wave function derived by applying the variation principle to a sufficiently large basis set (though it must be remembered that the quality of a wave function is not always measured very sensitively by its energy[41]).

To illustrate the effect of molecule formation on electronic charge distribution, we show in the Figure how the charge distribution in the carbon monoxide molecule (as calculated[42] from an extended-basis-set wave function[28]) differs from that in a hypothetical system consisting of a carbon atom and an oxygen atom at the same internuclear separation. According to earlier views based on less adequate evidence than is now available, the formation of a molecule was believed to be accompanied by an increase in electronic charge between the nuclei and a corresponding decrease beyond the nuclei. It is clear, however, from the Figure, and from similar diagrams for many other diatomic molecules[43] (homonuclear and heteronuclear) that there is (*i*) an increase in electronic charge around the internuclear axis in the region between the nuclei, (*ii*) a sharp decrease immediately around each nucleus, and (*iii*) an increase beyond each nucleus.

E. Dipole Moment.—The fact that an enlargement of the basis set does not necessarily improve the agreement between calculated and experimental values of molecular properties (other than molecular energies) is shown strikingly in the case of the dipole moment of carbon monoxide (Table 2). With the minimum basis set the absolute value is much too large, whereas with various extended sets[26–28] the sign is wrong. It has taken a 200-term configuration-interaction calculation[44] to produce a value (− 0·17 D) which gives reasonable agreement between theory and experiment. It should be pointed out that the dipole moment of carbon monoxide is unusually small, and depends very sensitively on internuclear distance; for these reasons it would perhaps be wrong to attach too much

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[35] A. D. McLean, *J. Chem. Phys.*, 1964, **40**, 243.

[36] R. H. Schwendeman, *J. Chem. Phys.*, 1966, **44**, 2115.

[37] L. Salem, *J. Chem. Phys.*, 1963, **38**, 1227; J. Goodisman, *ibid.*, 1963, **39**, 2397; R. H. Schwendeman, *ibid.*, 1966, **44**, 556; D. P. Chong, *Theor. Chim. Acta*, 1968, **11**, 205.

[38] R. E. Stanton, *J. Chem. Phys.*, 1962, **36**, 1298.

[39] G. G. Hall, *Phil. Mag.*, 1961, **6**, 249; *Adv. Quantum Chem.*, 1964, **1**, 241.

[40] J. Gerratt, *Ann. Reports(A)*, 1968, **65**, 3.

[41] J. Goodisman, *J. Chem. Phys.*, 1963, **38**, 304.

[42] R. F. W. Bader and A. D. Bandrauk, *J. Chem. Phys.*, 1968, **49**, 1653, 1666.

[43] R. F. W. Bader and A. K. Chandra, *Canad. J. Chem.*, 1968, **46**, 953.

[44] F. Grimaldi, A. Lecourt, and C. Moser, *Internat. J. Quantum Chem.*, 1967, **1**, S153.

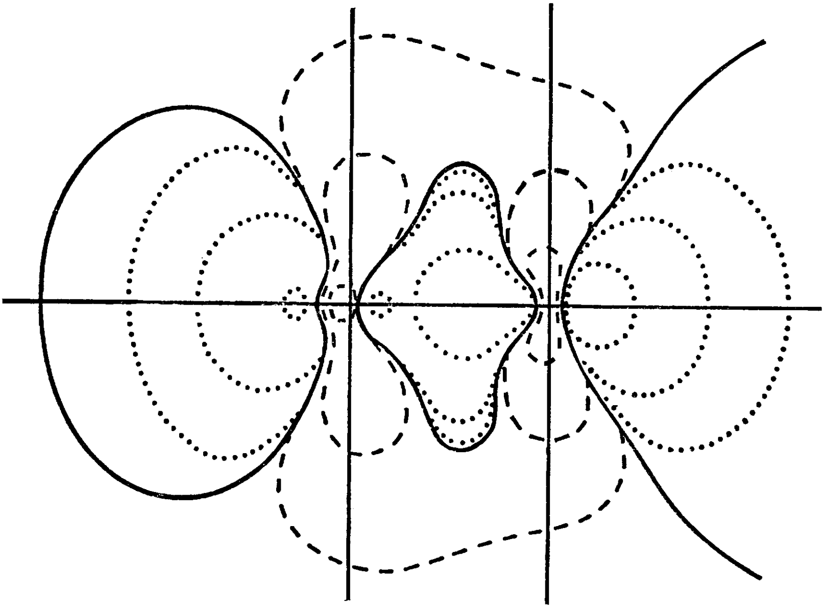

Figure *Electron density difference map for carbon monoxide. The horizontal line represents the internuclear axis, and its intersections with the vertical lines mark the positions of the carbon (left) and oxygen (right) nuclei.*
At each point $\Delta\rho = \rho_{CO} - (\rho_C + \rho_O)$, *where* ρ *is the electron density.*
Contours are plotted for $|\Delta\rho| = 0, 0{\cdot}001, 0{\cdot}01, 0{\cdot}1\ e\ \mathrm{B}^{-3}$. *Unbroken lines, dotted lines, and dashed lines represent contours on which* $\Delta\rho$ *is respectively zero, positive, and negative. In each zone* $|\Delta\rho|$ *decreases outwards from the internuclear axis. (All dotted lines and dashed lines form closed loops: they are shown incomplete in regions where, on the scale of the diagram, they merge into the adjacent unbroken lines.)*
[Redrawn from a more detailed map by Bader and Bandrauk, ref. 42.]

significance to the discrepancies associated with the single-configuration wavefunctions.

F. Electrical and Magnetic Properties.—Other quantities which have been calculated for the CO molecule include magnetic susceptibility,[45] magnetic shielding,[46] rotational magnetic moment,[47] polarisabilities,[48] and quadrupole

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[45] M. Karplus and H. J. Kolker, *J. Chem. Phys.*, 1963, **38**, 1263; J. R. de la Vega, D. Ziobro, and H. F. Hameka, *Physica*, 1967, **37**, 265.

[46] C. W. Kern and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 260.

[47] J. R. de la Vega and H. F. Hameka, *J. Chem. Phys.*, 1967, **47**, 1834.

[48] M. Karplus and H. J. Kolker, *J. Chem. Phys.*, 1963, **39**, 2011; J. M. O'Hare and R. P. Hurst, *ibid.*, 1967, **46**, 2356; A. D. McLean and M. Yoshimine, *ibid.*, 1967, **46**, 3682.

coupling constant.[49] Several methods[50] have been devised for calculating these quantities with LCAO wave functions. Lipscomb[51] and Gerratt[40] have provided comprehensive reviews of the subject, and have shown that reasonable agreement with experiment is usually obtained.

As far as multipole moments are concerned, both theoretical calculations and experimental determinations appear to be beset by considerable difficulties.[52]

G. Excited States.—From a basis set of *m* atomic orbitals, *m* linearly independent and orthogonal molecular orbitals are obtained automatically when the electronic energy is minimised with respect to the atomic-orbital coefficients. A $2N$-electron ground-state wave function in which all molecular orbitals are paired requires only the N molecular orbitals of lowest orbital energy, and thus the $(m - N)$ bigher-energy orbitals are superfluous ('virtual' orbitals). The simplest way of constructing wave functions for excited states is to replace one or more ground-state molecular orbitals by 'virtual' orbitals. This method has been used, with a variety of basis sets, by Lefebvre-Brion, Moser, and Nesbet[53] to calculate 'potential-energy' curves, spectroscopic constants, dipole moments, and dipole-moment derivatives for a number of low-lying excited states of CO.

A more thorough-going application of the variation principle requires that the atomic-orbital coefficients should be optimised afresh for each excited state. This procedure, which involves a surprising increase in technical difficulty, has been used by Huo[54] for CO (extended basis set), and by Sahni and Sawhney[55] for CO^+ (minimum basis set).

Calculations on excited states always give less satisfactory agreement with experiment than do calculations on ground states.

5 Improved and Adjusted Wave Functions

A. Configuration Interaction.—As pointed out in Section 4, single-determinant wave functions do not correspond to neutral dissociation products. In the case of certain molecules, as Das, Wahl, and others[56, 57] have shown for Li_2, F_2, and NaF, this difficulty can be overcome by adding to the wave function a second determinant based on another molecular configuration. The variation principle ensures, of

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[49] (*a*) J. W. Richardson, *Rev. Mod. Phys.*, 1960, **32**, 461; (*b*) H. Lefebvre-Brion, C. M. Moser, R. K. Nesbet, and M. Yamazaki, *J. Chem. Phys.*, 1963, **38**, 2311.

[50] M. Karplus, *Rev. Mod. Phys.*, 1960, **32**, 455; D. F. Tuan, S. T. Epstein, and J. O. Hirschfelder, *J. Chem. Phys.*, 1966, **44**, 431.

[51] W. N. Lipscomb, *Adv. Magn. Resonance*, 1966, **2**, 137.

[52] D. E. Stogryn and A. P. Stogryn, *Mol. Phys.*, 1966, **11**, 371.

[53] H. Lefebvre-Brion, C. M. Moser, and R. K. Nesbet, *J. Mol. Spectroscopy*, 1964, **13**, 418; R. K. Nesbet, *J. Chem. Phys.*, 1965, **43**, 4403.

[54] W. M. Huo, *J. Chem. Phys.*, 1966, **45**, 1554.

[55] R. C. Sahni and B. C. Sawhney, *Trans. Faraday Soc.*, 1967, **63**, 1.

[56] G. Das and A. C. Wahl, *J. Chem. Phys.*, 1966, **44**, 87; G. Das, *ibid.*, 1967, **46**, 1568; G. Das and A. C. Wahl, *ibid.*, 1967, **47**, 2934; B. Levy, *ibid.*, 1968, **48**, 1994.

[57] A. C. Wahl, P. J. Bertoncini, G. Das, and T. L. Gilbert, *Internat. J. Quantum Chem.*, 1967, **1**, S123.

course, that this reduces the calculated molecular energy. Calculated spectroscopic quantities are also improved. The change is most striking in F_2, for which the double-configuration wave function, unlike the simple LCAO wave function,[58] does not give a negative dissociation energy.

The nature of the double-configuration wave function is illustrated most simply by reference to Li_2, for which the single-determinant function is based on the configuration $1\sigma_g^2\,1\sigma_u^2\,2\sigma_g^2$. If this is combined with a second determinant based on the configuration $1\sigma_g^2\,1\sigma_u^2\,2\sigma_u^2$, and the linear-combination coefficient (a function of internuclear distance) is determined by applying the variation principle, the resulting wave function [of the type (5) in Section 2] becomes a wave function for two neutral Li atoms ($1s^2\,2s$) as $R \rightarrow \infty$. Exactly analogous wave functions have long been known for the hydrogen molecule.[3] (In H_2 a linear combination of σ_g^2 and σ_u^2 gives the correct behaviour on dissociation; σ_g^2 by itself does not.)

Wahl *et al.*[57] have given a general survey of configuration-interaction wave functions for diatomic molecules.

B. Open-shell Wave Functions.—Another way of improving single-configuration wave functions is to avoid the orbital pairing indicated in equations (1) and (2). General procedures of this type have been devised by Löwdin,[59] Goddard,[60] and Kaldor.[61]

C. Constrained Wave Functions.—In the integrals from which molecular properties are calculated, the integrands vary considerably from one point to another in the co-ordinate space. The manner in which different regions of a molecule are weighted in the integration depends upon the nature of the Schrödinger operator representing the molecular property. For some properties the regions nearest the nuclei are the most important, for others the regions furthest away. This is why even a very flexible wave function may, if optimised with respect to the energy, give disappointingly imprecise values for other quantities; whereas a poor wave function is almost certain to give poor results, a good wave function (in the variational sense) will not necessarily give good results.

For this reason early success in the precise calculation of a wide range of properties seems unlikely to be achieved merely by making variational wave functions more and more complicated. Mukherji and Karplus,[62] in an altogether different approach, have argued that if quite a simple energy-optimised wave function is adjusted so as to give the observed numerical values for some molecular properties, the adjusted wave function might be expected to give good values for other properties represented by integrals in which the same regions of the molecule are important. They re-varied some of the LCAO coefficients in Ransil's minimum-basis-set wave function[24] for HF, subject to the constraint that the

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[58] A. C. Wahl, *J. Chem. Phys.*, 1964, **41**, 2600.
[59] P.-O. Löwdin, *Phys. Rev.*, 1955, **97**, 1509.
[60] W. A. Goddard, *Phys. Rev.*, 1967, **157**, 73, 81; *J. Chem. Phys.*, 1968, **48**, 450, 5337.
[61] U. Kaldor, *J. Chem. Phys.*, 1968, **48**, 835.
[62] A. Mukherji and M. Karplus, *J. Chem. Phys.*, 1962, **38**, 44.

relevant integrals should give the experimental values for the dipole moment and the deuteron quadrupole coupling constant. This reduced the errors in the calculated diamagnetic and paramagnetic susceptibilities by more than half. The adjustment in the previously optimised LCAO coefficients necessarily raised the calculated energy, but by a mere 0·004%.

Variants and extensions of the procedure followed by Mukherji and Karplus have been formulated by other authors.[63]

6 Bibliography

To demonstrate the scope and the extent of strict wave-mechanical calculations on LCAO wave functions, we give in Tables 3—8 a list of the relevant publications in the period from 1960 to mid-1969 on systems of four or more electrons. It is clear that, in addition to energy, a very wide range of molecular properties can be calculated from LCAO wave functions (in some cases not very precisely as yet).

We include in these Tables many calculations which have been superceded by others of greater complexity. This is partly for the reason given at the end of Section 5, but mainly because the effects of varying orbital exponents, extending basis sets, and using multiconfiguration wave functions can be judged only by consideration of a substantial collection of numerical examples. We have made this collection as complete as possible.

It seems likely that in the next few years calculations will be carried out on polyatomic molecules much more complicated than those we list, and that work on diatomic molecules will normally go beyond the single-configuration LCAO approximation.

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[63] Y. Rasiel and D. R. Whitman, *J. Chem. Phys.*, 1965, **42**, 2124; D. P. Chong and Y. Rasiel, *ibid.*, 1966, **44**, 1819; W. B. Brown, *ibid.*, 1966, **44**, 567; C. P. Yue and D. P. Chong, *Theor. Chim. Acta*, 1968, **12**, 431; S. Fraga and F. W. Birss, *ibid.*, 1966, **5**, 398; S. Fraga and G. Malli, *ibid.*, 1966, **5**, 446.

Notes on Tables 3–6. In the columns headed 'Basis set' the first letter denotes the size:

M = minimum;
E = extended.

The second letter, if S, A, P, or M, refers to the atomic-orbital exponents:

S . . . . . determined arbitrarily, *e.g.* by Slater's Rules;
A . . . . . optimised for the free atom;
P . . . . . partially optimised for the molecule;
M . . . . . completely optimised for the molecule.

If the second letter is E, the wave function is formulated in elliptical co-ordinates.

The numbers in parentheses refer, for each atom, to the number of radially distinct orbitals of each symmetry type, in the order (σ, π, δ), the order of the atoms matching that in the chemical formula. For non-planar molecules, only the total number of atomic orbitals on each nucleus is listed. The letter C following the parentheses indicates a 'configuration-interaction' calculation.

In the case of FH, for example, MS(3,1)(1,0)C denotes a multiconfiguration wave function using the following minimum basis set of atomic orbitals, with the exponents determined by Slater's Rules:

F(σ): $1s$, $2s$, $2p_z$ (= $2p\sigma$);
F(π): $2p_x$, $2p_y$ (not radially distinct);
H(σ): $1s$;
H(π): nil.

For a wave function in elliptical co-ordinates only one set of numbers is required to specify the orbital symmetry types. (Such wave functions do not come strictly within the scope of this Review, but they are listed for comparative purposes.)

If a calculation is carried out for more than one geometrical configuration (more than one set of bond lengths and bond angles) the number is listed under the heading 'Additional calculations'. In the same column are noted calculations on excited states (e) and calculations on positive ions (i).

Letters in parentheses in the Reference columns denote papers which are concerned with excited-state wave functions and do not give details of the corresponding ground-state wave functions. Such reference letters in parentheses are given, quite arbitrarily, together with the first entry for each molecule.

In almost all cases, the internuclear distances (R) for which the molecular energies (E) and the dipole moments (μ) have been calculated are those determined experimentally. (To save space molecular dimensions are not given in Table 6.) The sign of the dipole moment is positive if the lighter nucleus is at the positive end.

Table 3 *Molecular energies (E) of homonuclear diatomic molecules**

Molecule	*Basis set*	$-E$ (H)	R (B)	*Additional calculations*	*Reference*
Li$_2$	MM(3,0)	14·842	5·051		*a*
	MM(3,0)C	14·852	5·051		*b*
	EP(15,3)C	14·899	5·25	8	*c*
	EP(17,6)C	14·903	5·07	10	*d*
Be$_2$	MM(3,0)	29·058	3·78		*a*
	MM(3,0)C	29·105	3·78		*b*
	EE(16,8)C	29·220	4·5		*e*
B$_2$	EE(10,8)C	49·145	3·0	10,e	*f*
C$_2$	MM(3,1)	75·224	2·3475		*a*(*n*)
	MM(3,1)C	75·319	2·3475		*b*
N$_2$	MS(3,1)	108·574	2·0675	e,i	*g*(*o*—*q*)
	MM(3,1)	108·634	2·068		*a*
	MM(3,1)	108·634	2·1	53,i	*h*
	MM(3,1)C	108·661	2·068		*b*
	EA(5,2)	108·785	2·068	e,i	*i*
	EA(7,3)	108·971	2·068	5	*j*
	EM(20,6)	108·993	2·068	16,i	*k*
O$_2$	MS(3,1)	149·092	2·2817	e,i	*g*
F$_2$	MM(3,1)	197·877	2·68		*a*
	MM(3,1)C	197·956	2·68		*b*
	EM(18,10)	198·768	2·68		*l*
	EP(18,10)C	198·838	2·68	6	*c*
P$_2$	ES(6,3)	679·166	3·58		*m*

*LCAO wave functions and potential-energy curves have been calculated for He$_2$, Ne$_2$, and Ar$_2$ (T. L. Gilbert and A. C. Wahl, *J. Chem. Phys.*, 1967, **47**, 3425).

[a] B. J. Ransil, *Rev. Mod. Phys.*, 1960, **32**, 239, 245; [b] S. Fraga and B. J. Ransil, *J. Chem. Phys.*, 1962, **36**, 1127; [c] G. Das and A. C. Wahl, *J. Chem. Phys.*, 1966, **44**, 87; [d] G. Das, *J. Chem. Phys.*, 1967, **46**, 1568; [e] C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, 1967, **47**, 4972; [f] C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, 1967, **46**, 3313; [g] R. C. Sahni and E. J. de Lorenzo, *J. Chem. Phys.*, 1965, **42**, 3612; [h] R. C. Sahni and B. C. Sawhney, *Internat. J.*

Quantum Chem., 1967, **1**, 251; [i] J. W. Richardson, *J. Chem. Phys.*, 1961, **35**, 1829; [j] R. K. Nesbet, *J. Chem. Phys.*, 1964, **40**, 3619; [k] P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.*, 1966, **44**, 1973; [l] A. C. Wahl, *J. Chem. Phys.*, 1964, **41**, 2600; [m] D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, 1967, **46**, 910; [n] R. K. Nesbet and P. F. Fougere, *J. Chem. Phys.*, 1966, **44**, 285; G. Verhaegen, *ibid.*, 1968, **49**, 4696; [o] G. Verhaegen, W. G. Richards, and C. M. Moser, *J. Chem. Phys.*, 1967, **47**, 2595.; [p] R. K. Nesbet, *J. Chem. Phys.*, 1965, **43**, 4403; [q] H. Lefebvre-Brion and C. M. Moser, *J. Chem. Phys.*, 1965, **43**, 1394.

Table 4 *Molecular energies (E) and dipole moments (μ) of diatomic hydrides*

Molecule	*Basis set*	$-E$ (H)	R (B)	μ (D)	*Additional calculations*	*Reference*
LiH	MM(3,0)(1,0)	7·970	3·015	− 5·92		*a*(*u*)
	MM(3,0)(1,0)C	7·984	3·015	− 5·57		*b*
	Ee(6,0)	7·987	3·02	− 6·035		*c*
	EM(12,0)(4,0)	7·987	3·015	− 6·002	16,i	*d*
	ES(4,0)(1,0)C	8·006	3·015	− 6·04		*e*
	EP(7,2)(3,1)C	8·017	3·02	− 5·89	3	*f*
	Ee(12,4)C	8·039	3·2		4	*g*
	Ee(7,3)C	8·041	2·99	− 5·96	2	*h*
	Ee(17,10,5)C	8·061	3·015	− 5·965		*i*
BeH^+	MA(3,1)(1,0)C	14·836	2·68		6	*j*
BeH	EM(12,0)(4,0)	15·153	2·538	− 0·282	16,i	*d*
	Ee(17,11,6)C	15·221	2·538	− 0·07	e	*k*
BH	MM(3,0)(1,0)	25·075	2·329	1·58		*a*
	MM(3,0)(1,0)C	25·090	2·329	1·53		*b*
	EM(12,0)(4,0)	25·131	2·336	1·733	16,i	*d*
CH^+	MA(3,1)(1,0)C	37·859	2·34		6	*j*
CH	EM(12,6)(4,2)	38·279	2·124	1·57	16,i*	*d*(*v*)
NH	MM(3,1)(1,0)	54·325	1·976	2·01		*a*(*v*)
	MM(3,1)(1,0)C	54·345	1·976	2·06		*b*
	EM(12,6)(4,2)	54·978	1·961	1·627	16,i*	*d*
OH	EM(12,6)(4,2)	75·421	1·8342	1·78	16,i	*d*
OH^-	EM(12,6)(4,2)	75·418	1·781	3·353	17	*l*
FH	MM(3,1)(1,0)	99·536	1·733	1·44		*a*(*w*)
	MM(3,1)(1,0)C	99·564	1·733	1·3		*b*
	EA(6,3)(3,2)	99·991	1·733	2·009	3	*m,n*
	EA(9,4)(3,2)	100·057	1·7328	1·827		*m*
	EM(8,4)(3,1)	100·058	1·7328	1·984	6,i	*o*
	EM(12,6)(4,2)	100·070	1·7328	1·942	16,i	*d*
	EM(12,7)(6,3)	100·071	1·7328	1·934		*p*
	Ee(19,17,7,1)C	100·257	1·733	1·649		*q*
NeH^+	EM(11,6)(5,2)	128·628	1·83		16	*r*
NaH	EM(12,6)(4,2)	162·393	3·566	− 6·962	15,i	*s*
MgH	EM(12,6)(4,2)	200·157	3·271	− 1·516	15,i	*s*
AlH	EM(12,6)(4,2)	242·463	3·114	0·17	15,i	*s*
SiH	EM(12,6)(4,2)	289·436	2·874	0·302	15,i*	*s*

Moleule	*Basis set*	*—E* (H)	*R* (B)	*μ* (D)	*Additional calculations*	*Reference*
PH	EM(12,6)(4,2)	341·293	2·708	0·538	15,i*	*s*
SH	EM(12,6)(4,2)	398·102	2·551	0·861	15,i	*s*
SH^-	EM(12,6)(4,2)	398·146	2·512	3·546	15	*l*
ClH	EA(9,4)(3,1)	459·804	2·4085	1·387	3,i	*t*
	EM(12,6)(4,2)	460·110	2·4087	1·197	15,i	*s*
	EP(17,10)(6,3)	460·112	2·4087	1·215		*p*

* Electron affinities calculated by similar calculations on negative ions (P. E. Cade, *Proc. Phys. Soc.*, 1967, **91**, 842).

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Table 5 *Molecular energies (E) and dipole moments (μ) of heteronuclear diatomic molecules*

Molecule	*Basis set*	*– E* (H)	*R* (B)	*μ* (D)	*Additional calculations*	*Reference*
Alkali-metal halides						
LiF	MA(3,1)(3,1)	106·381	2·85	3·43		*a*
	MP(3,1)(3,1)C	106·412	2·85			*b*
	EP(6,2)(9,4)	106·989	2·8877	6·297	13	*c*
	EP(7,3)(11,6)	106·992	2·8877	6·3	7	*d*
LiCl	EP(8,3)(14,7)	467·055	3·825	7·256	9	*e*
LiBr	EP(7,3)(18,10,2)	2579·89	4·0655		10	*f*
NaF	EP(13,6)(10,5)	261·379	3·628	– 8·367	9	*g*
NaCl	EP(13,6)(14,7)	621·457	4·4609	9·101	8	*h*
NaBr	EP(11,5)(18,10,2)	2734·29	4·728			*f*
KF	EP(18,8)(9,5)	698·685	4·1035		7	*i*
KCl	EP(15,7)(12,6)	1058·76	5·039		5	*f*
RbF	EP(21,11,2)(8,4)	3037·77	4·3653			*f*

Molecule	*Basis set*	*—E* (H)	*R* (B)	*μ* (D)	*Additional calculations*	*Reference*
Group II compounds						
BeO	EP(5,2)(8,4)	89·428	2·676		4,e	*j(bb)*
	EP(6,2)(10,5)	89·448	2·4377	7·29	10	*k*
	EP(10,4)(12,6)	89·454	2·4377	7·35	9	*d*
BeS	ES(5,2)(13,6)	412·097			e	*l*
MgO	EP(14,7)(12,6)	274·386	3·3052	9·18	8	*d(cc)*
CaO	EP(15,7)(12,6)	751·559	3·4412	11·48	7	*d*
SrO	EP(20,10,2)(7,3)	3206·23	3·6283	10·2	7	*d*
Group III compounds						
BN	MS(3,1)(3,1)	78·717	2·421	– 1·430	e	*m(dd)*
BF	MA(3,1)(3,1)	123·604	2·385	– 1·96		*a(ee)*
	MP(3,1)(3,1)C	123·676	2·385	– 1·13		*b*
	EA(7,3)(7,3)	124·140	2·385	– 0·668	5	*n*
	EP(7,3)(9,5)	124·166	2·391	– 0·945	8	*o*
	EP(11,6)(11,6)	124·167	2·391	– 0·88	7	*d*
AlF	EP(14,7)(11,6)	341·483	3·126	1·34	7	*d*
Group IV compounds						
CO^+	MM(3,1)(3,1)	111·956	2·075		57,i	*p*
CO	MA(3,1)(3,1)	112·326	2·132	– 0·592		*a,q(ff)*
	MS(3,1)(3,1)	112·344	2·132	– 0·730		*a,q*
	MM(3,1)(3,1)	112·392	2·132		72	*r*
	MP(3,1)(3,1)C	112·396	2·132	0·0872		*b*
	EA(7,3)(7,3)	112·759	2·132	0·397	5	*n*
	EP(8,4)(8,4)	112·786	2·132	0·274	7	*o*
	EP(11,6)(11,6)	112·789	2·132	0·28	7	*d*
CN^-	MA(3,1)(3,1)	91·927	2·18	– 1·84		*s*
CS	EA(7,3)(12,6)	435·330	2·9	1·6	3	*t*
SiO	EP(14,7)(11,6)	363·852	2·854	3·68	7	*d*
Group V compounds						
NF	MM(3,1)(3,1)	153·205	2·45		13,e,i	*u*
PN	EP(14,7)(11,6)	395·185	2·818	3·23	7	*d*
PO	ES(6,3)(3,1)	414·137	2·738	– 0·7	i	*v*
Transition-metal compounds						
ScO	EP(8,4,2)(3,2,1)	833·096	3·05	– 2·6	3,e	*w*
ScF	EP(10,5,2)(4,3)	858·545	3·31	– 4·64	e	*x*
TiN	EP(8,4,2)(3,2)	901·127	3·00	– 3·55	2,e	*y*
TiO	EP(8,4,2)(3,2)	921·542	3·0618	– 2·863	3,e	*z(gg)*
	EP(10,5,2)(4,3)	922·498	2·91	– 5·93	e	*x*
VO	EP(8,4,2)(3,2)	1015·89	2·91	– 3·61	3,e	*aa*

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Table 6 *Molecular energies (E) of polyatomic molecules*

Molecule	*Basis set*	− *E* (H)	*Additional calculations*	*Reference*
Group III compounds				
BH_3	MS(3)(1)	26·338		*a*
	MM(3)(1)	26·352	*	*b*
BH_4^-	MM(3)(1)	36·907		*c*
B_2H_6	MS(3)(1)	52·678		*a*
	MP(3)(1)	52·715		*b*
B_4H_4	MS(3)(1)	100·730		*d*
Group IV compounds				
(*a*) *Hydrides*				
CH_2	ES(6,0)(1,0)	38·904	13,e	*e*
CH_4	MS(3)(1)	40·114		*a,f*
	MM(3)(1)	40·128	3	*g*
	EA(11)(2)	40·181	3	*h*
	EP(9)(3)	40·205		*i*
C_2H_4	MS(3,1)(1,0)	77·834		*a*(*qq*)
	MS(3,1)(1,0)C	77·876	7,e,i	*j*
C_2H_6	MS(3)(1)	79·069	2	*a,k*
	MP(3)(1)	79·098	2	*l*
SiH_4	EA(6)(1)	290·519		*m*

Molecule	*Basis set*	−*E* (H)	*Additional calculations*	*Reference*
(*b*) *Acetylenes*				
C_2H_2	MA(3,1)(1,0)	76·544		*n*
	MS(3,1)(1,0)	76·617		*a*
	MM(3,1)(1,0)	76·678	e,i	*o*
	EP(11,6)(4,2)	76·854		*p*
CH_3CCH	MS(3,1)(1,0)(3,1)(3,1)(1,0)	115·583		*q*
LiCCH	EP(6,3)(9,5)(9,5)(4,2)	83·731	4	*r*
FCCH	EP(9,5)(9,5)(9,5)(4,2)	175·724		*s*
ClCCH	EP(12,6)(8,4)(8,4)(4,2)	535·767		*s*
NCCCH	EP(7,3)(7,3)(7,3)(7,3)(4,2)	168·578		*s*
(*c*) *Cyanides*				
HCN	MA(1,0)(3,1)(3,1)	92·547		*t,u*
	MS(1,0)(3,1)(3,1)	92·590		*a*
	EP(4,2)(11,6)(11,6)	92·915	12	*s*
C_2N_2	MA(3,1)(3,1)	183·982		*v*
	EP(9,5)(9,5)	184·657		*p*
NCO^-	MA(3,1)(3,1)(3,1)	166·459		*t*
	EP(9,5)(9,5)(9,5)	167·270		*s*
HNCO	MA(1,0)(3,1)(3,1)(3,1)	167·076		*t*
FCN	EP(9,5)(9,5)(9,5)	191·780		*s*
SCN^-	EP(12,6)(8,4)(8,4)	489·911		*s*
ClCN	EP(12,6)(8,4)(8,4)	551·825		*s*
(*d*) *Others*				
C_3	MA(3,1)	113·088		*w*
	EA(3,2)(6,1)(3,2)	113·165		*x*
C_4	MA(3,1)	150·844	e	*y*
CO_2	MA(3,1)(3,1)	186·843		*n*
	EP(4,1)(6,1)	187·076		*z*
	EP(8,4)(8,4)	187·723	4	*s*
OCS	MA(3,1)(3,1)(5,2)	508·492		*aa*
	EP(8,4)(8,4)(12,6)	510·331		*s*
H_2CO	MS(1,0)(3,1)(3,1)	113·450		*bb,cc*
	MS(1,0)(3,1)(3,1)	113·427		*bb,dd*

Molecule	*Basis set*	*− E* (H)	*Additional calculations*	*Reference*
Group V compounds				
NH_3	MS(3)(1)	56·005		*a*
	EA(6)(1)	56·099	2,i	*ee*
PH_3	ES(6)(1)	341·309		*ff*
N_3	MA(3,1)	162·542		*w,t*
	EA(3,2)(5,1)(3,2)	162·705		*gg*
HN_3	MA(1,0)(3,1)	163·224		*t*
N_2O	EP(9,5)(9,5)	183·757	9	*s*
NO_2^+	MA(3,1)(3,1)	202·901		*w*
	EA(5,1)(3,2)	203·108		*gg*
NO_2^-	MA(3,1)(3,1)	203·174		*hh*
	EA(6,2)(6,2)	203·986		*ii*
NOF	MS(3,1)(3,1)(3,1)	227·708		*hh*
PO_2^-	ES(6,3)(3,1)	488·77		*jj*
Group VI compounds				
H_2O	MS(1)(3)	75·681		*kk*
	EP(3)(7)	76·005		*ll*
H_2O_2	MA(1,0)(3,1)	150·157	8	*mm*
	MP(1,0)(3,1)	150·223	7	*nn*
O_3	MA(3,1)	223·479		*hh*
OF_2	MA(3,1)(3,1)	272·425		*hh*
	EA(6,2)(6,2)	273·526		*ii*
H_2S	EA(1)(6)	397·842		*m*
Group VII compounds				
HF_2^-	MA(1,0)(3,1)	198·283		*w*
	EA(3,1)(4,2)	199·393		*oo*
	EP(4,3)(8,4)	199·573	21	*s*
Transition-metal compounds				
ScH_3NH_3	MA(8)(1)(3)(1)	816·204		*pp*
TiH_3F	MA(8)(1)(3)	947·464		*pp*

• B—H distance treated as variational parameter.

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Tables 7 and 8, on the following pages, list papers in which various molecular properties are calculated from previously published wave functions.

Table 7 *Literature references to calculations of various molecular quantities*

Diatomic molecules

Molecule	*Electron density*	*Magnetic properties*	*Polarisabilities*	*Quadrupole coupling constant and/or dipole moment*	*Spectroscopic quantities*
LiH	*a—f*	*q—y*	*w,kk,ll*	*nn,oo*	*vv—xx*
BeH	*c*			*nn*	
BH	*c—f*	*u—x,z,aa*		*nn*	*ww xx*
CH	*c,g*	*bb*		*nn*	
NH	*c—f*	*u*		*nn*	*ww*
OH	*c*			*nn*	
FH	*b—f,k,n*	*s—w,cc,dd*	*dd,kk,ll*	*nn—pp*	*vv—xx*
NaH,MgH,AlH,SH,SiH,PH	*o*			*nn*	
ClH	*o*			*nn,pp*	
Li_2	*e,f,i—m*	*s—v,ee,ff*	*kk,ll*	*qq,rr*	*vv,yy*
Be_2	*e,f,j*	*v,ff*			*vv,yy*
B_2,O_2	*i,j*				
C_2	*f—j*	*v,ff*			*yy,zz*
N_2	*e—k,p*	*r—v,ff,gg*	*kk,ll*	*qq*	*vv,yy*
F_2	*e,f,i—l*	*s—v,ff,hh*	*ll,hh*		
LiF	*e,f,h,k,ss*	*s—v,ii*	*kk*		*ww*
BeO	*h*				
BeF					*aaa*
MgF					*bbb*
BN	*d*				
BF	*e—h,p*	*u,v,aa,ii*	*ll*		*ww*
CO	*d—h,p*	*t—v,ii,jj*	*kk,ll,mm*	*jj,qq,tt*	*ww*
NO					*uu,ccc*

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Table 8 *Literature references to calculations of various molecular quantities*

Polyatomic molecules

Molecule	*Electron density*	*Magnetic properties*	*Quadrupole coupling constant*	*Internal rotation or inversion barrier*
B_2H_6		*a*		
CH_4		*b,c*	*d*	
C_2H_2	*e,f*	*g*	*h*	
C_2H_4		*g,i*		
C_2H_6		*g*	*j*	*k*
HCN	*e,l,m*		*j,n*	
C_2N_2	*e,l,m*			
C_3,C_4	*e*			
CO_2	*f*			
HCHO		*o*	*o*	
SCO		*p*		
NH_3		*c*	*q*	*r*
N_3^-			*h*	
N_2O		*s*	*s*	
H_2O		*c*		
H_2O_2		*c*		*r*
HF_2^-			*h*	
FCN	*m*		*n*	
ClCN, HCCCN, OCN^-, SCN^-			*n*	

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