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Non-empirical Calculations of the Force Constants for Small Molecules

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The review gives a consistent description and analysis of the ideas underlying the determination of potential constants (coefficients of the potential function formulated as a power series in terms of generalised coordinates) for diatomic and simple monatomic molecules using quantum-chemical methods. Calculations for specific molecules of greatest interest both theoretically and practically are briefly considered; the results of these calculations are presented in the form of tables.
The bibliography includes 80 references.

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I. INTRODUCTION

The review deals with the present state of the solution of the problem of evaluation of a potential function of the type

$$V = \frac{1}{2!}\sum_{\alpha,\beta} K_{\alpha\beta} q_\alpha q_\beta + \frac{1}{3!}\sum_{\alpha,\beta,\gamma} K_{\alpha\beta\gamma} q_\alpha q_\beta q_\gamma + \frac{1}{4!}\sum_{\alpha,\beta,\gamma,\delta} K_{\alpha\beta\gamma\delta} q_\alpha q_\beta q_\gamma q_\delta + \cdots \quad (1)$$

where $K_{\alpha\beta}$ are harmonic (quadratic) molecular force constants, $K_{\alpha\beta\gamma}$ and $K_{\alpha\beta\gamma\delta}$ are anharmonic (cubic and quadratic respectively) force constants, and q_α are generalised coordinates.

The determination of force constants by the solution of the vibrational–rotational problem involves a fundamental difficulty—the number of unknowns is greater in the majority of cases than the number of equations which may be formulated from the available experimental data.

Therefore the approach based on solving the electronic problem in the adiabatic approximation [1], according to which

$$K_{\alpha\beta} = \left(\frac{\partial^2 E}{\partial q_\alpha \partial q_\beta}\right)_e,\quad K_{\alpha\beta\gamma} = \left(\frac{\partial^3 E}{\partial q_\alpha \partial q_\beta \partial q_\gamma}\right)_e,\quad K_{\alpha\beta\gamma\delta} = \left(\frac{\partial^4 E}{\partial q_\alpha \partial q_\beta \partial q_\gamma \partial q_\delta}\right)_e, \quad (2)$$

is of undoubted interest in connection with the possibility, in principle, of eliminating the above difficulty and also the possibility of achieving a deeper understanding of the nature of dynamic interactions in molecules.

At the present time the principal aim is of course to develop methods for the calculation of force constants and to test their effectiveness on comparatively simple systems, not merely to secure new data for the force constants of specific molecules.

Thus in Eqn. (2) E is the total energy of a molecular system containing N nuclei with charges $Z_1, \ldots, Z_N$ and n electrons†:

$$E = E_e + E_N, \quad (3)$$

where

$$E_e = \langle \Psi_1 H_e \Psi \rangle \quad (4)$$

is the energy of the electronic shells in the field of nuclei with the given configuration and

$$E_N = \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (5)$$

is the energy of the electrostatic interaction of the nuclei, excluding the kinetic energy of the motion of the latter.

In Eqns. (4) and (5), $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n; \mathbf{R}_1, \ldots, \mathbf{R}_N)$ is the electronic wave function and H_e is the electronic Hamiltonian:

$$H_e = \sum_{i=1}^{n}\left(-\frac{1}{2}\Delta_i - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}\ ; \quad (6)$$

$R_{\alpha\beta} = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$ is the distance between the nuclei α and β, $r_{\alpha i} = |\mathbf{R}_\alpha - \mathbf{r}_i|$ the distance between the ith electron and the α nucleus, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ the distance between the ith and jth electrons, the nuclear configuration being described by the vectors $\mathbf{R}_1, \ldots, \mathbf{R}_N$ and the electron configuration by $\mathbf{r}_1, \ldots, \mathbf{r}_n$.

In the adiabatic approximation function (3) plays the role of a potential energy V of the relative atomic vibrations employed in the theory of molecular vibrations [3]. Thus at equilibrium the total energy may be represented by the series (1) and the problem of determining the force constants of the molecule in the given electronic state now reduces to the calculation of the derivatives of the total energy of the system with respect to generalised coordinates.

II. NUMERICAL METHODS FOR THE CALCULATION OF FORCE CONSTANTS

We shall consider initially the possibilities which arise in the solution of the problem of the Hartree–Fock–Roothaan self-consistent field (SCF) method [4,5]. The applications and discussion of various aspects of the self-consistent field method in the calculation of other properties of atoms and molecules may be found in Sokolov's review [6].

Using the Hartree–Fock method, a number of investigators have calculated the electronic energy for various nuclear configurations (in the vicinity of the equilibrium configuration) for diatomic and small polyatomic molecules. Such calculations make it possible to plot potential curves and surfaces and to determine the potential constants by numerical differentiation. It must be emphasised that more calculations of this kind, particularly recently, became possible with increased availability of computers.

A typical example of such an approach, usually referred to in the literature as "traditional", is the calculation of

†The formulae and the numerical results in the review are quoted in atomic units (a.u.), unless otherwise stated [2].

the force constants of diatomic molecules in the ground and excited states by Fraga and Ransil [7] carried out on the basis of the self-consistent field functions in both the one-determinant approximation and taking into account the interaction between the configurations (CI).

In their studies the potential curve is approximated by a third degree polynomial in R of the form

$$E = a + bR + cR^2 + dR^3, \quad (7)$$

the coefficients of which are determined by the least square solution of a set of equations of the type of Eqn. (7) for various values of R and the corresponding E. Since the expressions for the vibrational–rotational constants (ω_e, $\omega_e x_e$, B_e, α_e, and $K_{\alpha\beta}$) can be obtained by solving the corresponding Schrödinger equation with a potential function of the type [8]

$$E = a - fR^2 - gR^3, \quad (8)$$

Fraga and Ransil converted the coefficients of Eqn. (7) into those of Eqn. (8) by the formulae $g = -d$ and $f = (c^2 - 3bd)^{1/2}$. This numerical analysis of the potential curves does not differ in principle from that employed in the majority of investigations. The only difference lies either in the choice of the approximating function or in the method of estimation of the similarity of the functions over a certain interval, etc.

The agreement between the $K_{\alpha\beta}$ calculated in the one-determinant approximation and the experimental values [8] is satisfactory despite the fact that the molecular orbitals (MO) include only the internal and Slater valence atomic orbitals (AO) and the polynomial (7) is restricted to the third power of R (Table 1); the deviations from the experimental values lie in the range 8–20% for the molecules H_2, LiH, and Li_2.

An interesting result was obtained by Nesbet in Hartree–Fock calculations for a number of diatomic molecules [9,10]; an appreciable improvement in the calculation of the force constants in the one-configurational approximation arises when polarisation and deformation of atomic orbitals as a consequence of their intramolecular environment are postulated, in contrast to the hypothesis that the molecular orbitals may be constructed as linear combinations (LC) of undeformed atomic orbitals. This effect may be described by including a greater number of basis functions than in the minimum set, with higher angular quantum numbers than for separated atoms.

To illustrate this, we shall quote the results of this type of calculation for the $^1\Sigma^+$ states of the isoelectronic molecules N_2, CO, and BF carried out by Nesbet [11]; in this case the potential curve is approximated by a series in terms of Chebyshev functions.

Then the analytical expression obtained for the potential curve can be put in the form

$$E = b_0\xi^2 \sum_k b_k \xi^k, \quad (9)$$

where $\xi = (R - R_e)/R_e$. Dunham [12] solved the vibrational–rotational Schrödinger equation with a potential defined by an expression of type (9). This makes it possible to find, using the formulae obtained, all the fundamental spectroscopic constants for a given bound state. Such numerical analysis of the potential curve is usually referred to as the Dunham analysis.

Table 1 shows that there is significant agreement with the experimental force constants. For N_2 as an example, it is seen that the constant $K_{\alpha\beta}$ is somewhat improved compared with the values calculated with the aid of the minimal basal set.

Satisfactory agreement with experiment was obtained also for the F_2 molecule by Wahl [13], who likewise employed the Hartree–Fock–Roothaan procedure in the derivation of the potential curve with subsequent Dunham analysis leading to the force constants. It should be noted that this study is the first in a series designed by the author and his coworkers to obtain Hartree–Fock analytical wave functions for the ground and certain excited states of diatomic molecules. They believe that the calculations should provide a foundation for a critical analysis of the theory of electronic structures of small molecules. Thus the third paper [14] of this series presents the calculations of the wave functions of N_2^+ and N_2 in the ground and excited states with various forms of basis sets. All the calculations were made for a large number of internuclear distances, which makes it possible to calculate the force constants (Table 1). To eliminate computational errors, several polynomial approximations were made varying the number (from 4 to 10) and type of points [15] taken for the Hartree potential curve. The discrepancies between the calculated spectroscopic constants and experiment range from several per cent to several tens per cent and those for the force constant are in the range 34–64%.

Comparison of the potential curves with experiment, carried out in the above investigations and in the work of Leies [16] for the H_2 molecule (the calculation was based on the Hartree–Fock function obtained by Kolos and Roothaan [17]), suggests [18] that the curves are relatively congruent in the vicinity of equilibrium (and when $R < R_e$); the difference in their behaviour increases at larger internuclear distances. In turn, the results of the calculations for the force constants and certain other vibrational–rotational constants are fully consistent with the form of the potential curves. Thus the Hartree–Fock potential increases more rapidly from the point of equilibrium ($K_{\alpha\beta}$ >) but shows a smaller anharmonicity ($\omega_e x_e$ <) than the experimental potential. Such behaviour of the Hartree–Fock potential curves is evidently due to the following factors: the Hartree–Fock molecular orbitals lead to an incorrect dissociation limit for the majority of molecules, i.e. the molecules dissociate to give a series of neutral and ionic atomic states; moreover, the Hartree–Fock potential does not include the correlation energy, which is partly the reason for the effect described above.

Yoshimine [20] shows that, from the standpoint of these factors, the introduction of a scale factor into the wave function and its variation as a function of R to improve the force constants [19] is not particularly useful [although the appropriate variation of the scale factors does in fact alter these constants in the required direction, the change is only slight (Table 1)]. Huo's use of even more extended sets [21] (CO and BF molecules), compared with the basis sets [11], and the optimisation of the scale factors does not lead to a significant improvement of the force constants.

Before proceeding to studies in which attempts were made to improve the E_{H-F}, mention should be made of a very interesting study by Goodisman [22], who showed that the force curve (obtained directly from the expectation value of the one-electron operator $\partial H/\partial R$) leads to better results for $K_{\alpha\beta}$ than the energy curve calculated on the basis of Hartree–Fock functions with limited-basis of functions of the James and Coolidge type, namely the approximation of the energy curve by a parabola in the vicinity of R_e yields the force constant $K_{\alpha\beta} = 0.3795$ a.u. and the calculated values $R_e = 1.385$ a.u. and $\omega_e = 4458\ cm^{-1}$; numerical analysis of the force curve gives $K_{\alpha\beta} = 0.3727$ a.u., $R_e = 1.394$ a.u., and $\omega_e = 4417\ cm^{-1}$

Table 1. Force constants of molecules.

Molecule	Method of calculation of f.c.	Force constants (f.c.), a.u. quadratic theor.	quadratic expt *	cubic theor.	cubic expt	quartic theor.	quartic expt	Refs.
H_2^+	numerical	0.0987[a]	0.1006	—	—	—	—	7
He_2^+		0.2835	0.2005	—	—	—	—	7
H_3		0.4091	0.369	—	—	—	—	7
H_2		0.3994	—	—	—	—	—	16
H_2		0.3968[a] 0.3387[c] 0.3689[d]	—	—	—	—	—	28
LiH		0.0771[a]	0.0659	—	—	—	—	7
LiH		0.048[e]	—	—	—	—	—	29
Li_2		0.0121[a] 0.0135[c] 0.0136[d]	0.0141	—	—	—	—	28
Li_2		0.0151[a]	—	—	—	—	—	7
B_2		0.3042	0.2260	—	—	—	—	33
HF		0.9237[a]	0.6204	—	—	—	—	7
HF		0.6809[b]	—	—	—	—	—	7
N_2^+		1.634[a]	1.291	—	—	—	—	7
N_2^+		1.751[b]	—	−2.135	−1.819	1.922	1.580[z]	14
N_2		2.340[a]	1.474	—	—	—	—	7
N_2		1.964[f]	—	—	—	—	—	11
N_2		1.974[b]	—	−2.964	−2.012	4.279	1.792[z]	14
CO		1.442	1.222	—	—	—	—	11
CO		1.533[g]	—	—	—	—	—	21
BF		0.496	0.518	—	—	—	—	11
BF		0.590	—	—	—	—	—	21
BH		0.300[b]	0.195	—	—	—	—	31
CO		1.353[a] 1.070[b]	—	—	—	—	—	26
LiF		0.2225[h]	0.1800	—	—	—	—	19
		0.2223[i]	—	—	—	—	—	
BeO		0.6598[h]	0.6200	—	—	—	—	20
		0.6598[i]	—	—	—	—	—	
C_2		0.513[b]	0.782	—	—	—	—	32
F_2		0.927[a] 0.511[b]	0.304	—	—	—	—	7
F_2		0.538[b]		−0.696	−0.435	0.566	0.345[z]	13
F_2		0.6047[a] 0.1652[c]	—	—	—	—	—	28
H_3		K_{R_1}=0.288[b]	—	—	—	—	—	31
		K_{R_2}=0.023	—	—	—	—	—	
		K_{R_3}=0.05	—	—	—	—	—	
H_2O		K_{RR}=0.616[k]	0.543	—	—	—	—	31
		$K_{RR'}$=−0.04	−0.0065	—	—	—	—	
		$K_{R\varphi}$=−0.022	0.0149	—	—	—	—	
		$K_{\varphi\varphi}$=0.055	0.0489	—	—	—	—	
H_2O		K_{RR}=0.496[k]	—	—	—	—	—	33
		$K_{RR'}$=−0.0064	—	—	—	—	—	
		$K_{R\varphi}$=0.024	—	—	—	—	—	
		$K_{\varphi\varphi}$=0.056	—	—	—	—	—	
H_2	analytical	0.6032[j]	—	—	—	—	—	37
		0.4085[k]	—	—	—	—	—	
LiH		0.0250[j]	0.0659	—	—	—	—	35
BeH		0.0796	0.145	—	—	—	—	
BH		0.207	0.195	—	—	—	—	
CH		0.319	0.281	—	—	—	—	
NH		0.455	0.387	—	—	—	—	
OH		0.554	0.498	—	—	—	—	
H_2O		K_{RR}=0.7269[j]	—	—	—	—	—	38
		$K_{RR'}$=−0.038	—	—	—	—	—	
		$K_{R\varphi}$=0.0183	—	—	—	—	—	
		$K_{\varphi\varphi}$=0.0593	—	—	—	—	—	
NH_3		K_{RR}=0.579[k]	0.442	—	—	—	—	39
		$K_{RR'}$=−0.0135	0.0064	—	—	—	—	
		$K_{\varphi\varphi}$=0.0552	0.0411	—	—	—	—	
		$K_{\varphi\varphi'}$=−0.0019	−0.0039	—	—	—	—	
		$K_{R\varphi}$=0.0289	0.0084	—	—	—	—	
		$K_{R\varphi'}$=−0.0064	0.0295	—	—	—	—	
CH_4		K_{RR}=0.470	0.347	—	—	—	—	39
		$K_{RR'}$=−0.0141	0.0087	—	—	—	—	
		$K_{\varphi\varphi}-2K_{\varphi'\varphi}+K_{\varphi\varphi'}$=0.0263	0.0315	—	—	—	—	
		$K_{\varphi\varphi}-K_{\varphi\varphi'}$=0.0604	0.0295	—	—	—	—	
		$K_{R\varphi}-K_{R\varphi'}$=0.0135	0.0096	—	—	—	—	

Table 1 (cont'd).

Molecule	Method of calculation of f.c.	Force constants (f.c.), a.u. quadratic theor.	quadratic expt *	cubic theor.	cubic expt	quartic theor.	quartic expt	Refs.
H_2	analytical	0.3241[a] 0.2487[e]	—	—	—	—	—	40
		0.0590[a] 0.0474[e]	—	—	—	—	—	40
		0.0154[l]	—	—	—	—	—	29
Li_2		0.0103	0.0109	—	—	—	—	41
Na_2		0.0051	0.0064	—	—	—	—	
K_2		0.0437	0.0507	—	—	—	—	
NaH		0.0263	0.0360	—	—	—	—	
KH		0.0730	—	—	—	—	—	
LiH		0.361[m]	—	−1.193	−1.264	—	—	
H_2		0.0135	—	−0.0144	−0.0186	—	—	41, 42
Li_2		0.0097	—	−0.0085	−0.0107	—	—	
Na_2		0.499	—	−1.287	−1.299	—	—	
F_2		0.0940[n]	—	—	—	—	—	
H_2^+ I		0.0414	—	—	—	—	—	
II		0.343[o]	—	—	—	—	—	
H_2 I		0.863	—	—	—	—	—	43, 44
II		0.549[p]	—	—	—	—	—	
H_2 I		0.554	—	—	—	—	—	
II		0.434[q]	—	—	—	—	—	
H_4 I		0.689	—	—	—	—	—	
II		0.294[r]	0.368	—	—	—	—	45
H_2 I		−0.095	—	—	—	—	—	
II		0.293[s]	—	—	—	—	—	
H_2 I		−0.065	—	—	—	—	—	
II		0.391[t]	—	−1.30	−1.258	—	—	
H_2 I		0.337	—	−1.6	—	—	—	45
II		0.450[u]	—	−1.30	—	—	—	
H_2 I		0.400	—	−1.37	—	—	—	
II		0.374[v]	—	−1.40	—	—	—	
H_2 I		0.336	—	−1.15	—	—	—	
II		0.217[w]	—	−1.21	—	—	—	46
H_2		0.265	—	−0.92	—	—	—	
		0.290	—	−1.02	—	—	—	
H_2I		0.356[m]	—	−1.294	—	—	—	47
Li_2I		0.0122	0.0141	−0.0150	−0.0188	—	—	
LiH		0.0726[a]	0.0659	−0.107	−0.116	0.154	0.154	
BH		0.219	0.195	−0.489	−0.501	0.990	0.997	
CH		0.198	0.281	−0.542	−0.860	1.287	2.056	23,48,49
NH		0.233	0.387	−0.789	−1.334	2.013	3.570	
OH		0.268	0.499	−1.068	−1.817	2.929	5.121	

Remarks: [a]The Hartree–Fock–Roothaan function calculated in terms of the one-determinant approximation. [b]Configuration interaction taken into account. [c]Two configurations only (TCO). [d]Optimised valence configuration (OVC). [e]Configuration interaction taken into account to a limited extent. [f]Extended basis set compared with c^7. [g]Basis set extended still further (compared with c^{11}). [h]One-determinant non-scaled wave function. [i]One-determinant scaled function. [j]One-determinant one-centre function. [k]One-centre function including configuration interaction. [l]Calculated from Eqn. (12). [m]Simple wave function of the molecular orbital type. [n]Wave function ($1S_a + 1S_b$) calculated on the basis of the virial theorem (I) and the Hellmann–Feynman theorem (II). [o]Wang function. [p]Coulson function. [q]Weinbaum function. [r]Non-scaled Heitler–London wave function. [s]Ditto for the molecular orbital wave function. [t]Scaled Wang wave function; [u]Coulson function; [v]Weinbaum function; [w]On the basis of a variational-perturbation scheme; [z]the anharmonic force constants for certain molecules were calculated by the authors of the review (they are not quoted in the relevant papers) in those cases where the original authors give an insufficiently complete set of spectroscopic constants.

*The experimental values were taken from the references given in column 9.

(experiment gives $K_{\alpha\beta} = 0.3680$ a.u., $R_e = 1.401$ a.u., and $\omega_e = 4440\,cm^{-1}$). The results of this investigation and also the present authors' calculations[23] confirm the conclusion that, when the approximate Hartree–Fock function is close to the true Hartree–Fock function, one may expect a second-order perturbation error in the expectation value of the one-electron operator[24,25].

When account is taken of configuration interaction within the framework of the self-consistent field method, which leads to a correct dissociation limit, the force constants are improved provided that molecular orbitals with higher angular quantum numbers compared with the ground molecular orbital are included in the additional configurations.

Limited allowance for configuration interaction does in fact lead to a correct dissociation limit, but the force constants are not always improved. For example the inclusion by Fraga and Ransil[7] of additional configurations with the ground configuration resulted in a considerable improvement of the quadratic force constants of molecules such as HF and F_2, for which π configurations were included in the calculation (the error in the case of the one-determinant approximation is 49% for HF and 205% for F_2); however, poorer values of $K_{\alpha\beta}$ were obtained for H_2, LiH, and Li_2, since molecular orbitals with higher angular quantum numbers than the ground molecular orbital were not included in the additional configurations of the molecules. This was also shown by Moser, Nesbet, and others[26-28] in Hartree–Fock calculations of the spectroscopic constants of the molecules H_2, CO, LiF, Li_2, and F_2, among which the last merits a more detailed consideration. In their study the wave function with configuration interaction, which is of the form

$$\Psi = \sum_k d_k \Phi_k ,$$

contains several optimised configurations obtained by replacing one of the σ orbitals of the ground configuration by orbitals of a different type. The method is based on a model according to which, when a molecule is formed from Hartree–Fock atoms or ions initially at infinite separation, changes occur mainly in the valence orbitals. This factor is taken into account by the introduction of optimised valence configurations (OVC), which are constructed by the promotion of the valence electron pair from the ground state to an allowed "excited" orbital. By minimising the total energy and the energy of the optimised valence configurations, equations defining the best values of d_k and the orbital coefficients were obtained. The calculations were made for the molecules H_2, Li_2, and F_2, only two configurations being optimised in the last case. We may note that in all cases the molecules dissociate into two Hartree–Fock atoms (Figs. 1 and 2). Dunham analysis gives, particularly for the optimised valence configurations in the case of the H_2 and Li_2 molecules, fairly satisfactory values of $K_{\alpha\beta}$ (Table 1). Evidently this method is very promising for the calculation of spectroscopic constants by the numerical analysis of the potential curve, since it is based on a thoroughly developed expansion technique whilst retaining the simplicity and clarity of the shell model [moreover, the restriction to valence-excited configurations makes it possible to extend the method to systems with a larger number of atoms and to obtain a potential curve approximately congruent with the experimental curve for $R > R_e$ (Figs. 1 and 2), which shows that the correlation effects are partially taken into account]. Somewhat poorer results were obtained for F_2, compared with the other molecules, because the orbitals of the skeleton include orbitals such as $1\pi_u$ and $1\pi_g$, which are known to be of the valence type.

Among the earlier studies dealing with the LCAO-SCF method, with a limited allowance for configuration interaction, mention should be made of the work of Karo and Olson[29] (LiH) and Higuchi[30] (CH), the results of which also confirm the conclusion that molecular orbitals with higher quantum numbers than the ground orbital must be included in the additional configurations, and also the work of Boys et al.[31], where the force constants of the molecules BH and H_2O and the transition complex H_3 (the force constants of H_3 are not observed physically but are necessary for the prediction of reaction rates) were determined by the LCAO-SCF method with allowance for configuration interaction.

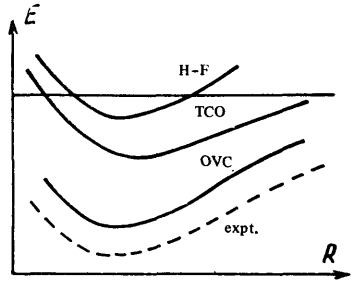


Figure 1.

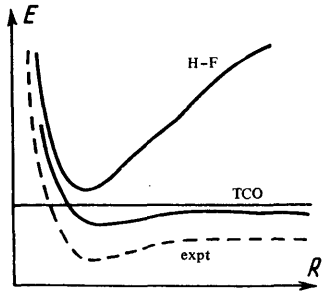


Figure 2.

Table 1 lists the force constant of the BH molecule obtained on the basis of a wave function, representing a linear combination of 23 Slater determinants and calculated for three internuclear distances, and the harmonic force constants of the H_2O molecule (in terms of the valence force system of coordinates[3]), the wave function of which was represented by a linear combination of 96 Slater determinants and calculated for seven nuclear configurations. The results are fully satisfactory for the diagonal force constants. The inconsistency of the results for the non-diagonal constants of H_2O both in magnitude and in sign can be accounted for largely by the errors in the derivation of the interpolation polynomial for the points at which the energy of the corresponding nuclear configuration was calculated.

The improvement of the Hartree–Fock calculations of the force constants by the introduction of configuration interaction has also been demonstrated in a recent investigation by Nesbet[32] of the electronic structure of C_2, which is the first of a series dealing with the study of the potential curves for the ground and certain excited states of the isoelectronic molecules C_2, BN, BeO, LiF, HeNe, and HNa. Here configuration interaction is introduced in two different ways: (1) two possible states which may be formed from four valence orbitals are considered and (2) two different orbital basis sets with six valence molecular orbitals are employed. Analysis of the potential curves shows a quantitative agreement between the experimental and calculated force constants. It is interesting that the statistical relations discovered by comparing the values obtained with experiment permit the prediction of the force constants of hitherto unobserved bound states, which are of interest, for example, for elucidating how molecules in an excited electronic state interact.

In concluding this review of numerical methods for the calculation of force constants, mention should be made of a number of studies[33–39] in which an interpolation procedure was also used to calculate the $K_{\alpha\beta}$, mainly for polyatomic molecules, but where the energies of various nuclear configurations were calculated using the one-centre approximation[36], which constitutes a variety of LCAO. A characteristic feature of the method is the employment of a basis set of functions centred on the same point, which makes it possible to avoid the calculation of many-centre integrals.

It should be noted that for hydrides of the type AH and AH_n the one-centre model both in the one-determinant approximation and with allowance for configuration interaction is very useful for the calculation of the quadratic force constants (Table 1). The one-centre approximation will be considered in greater detail below (p. 200 and p. 201) for reasons which will become clear later.

Summarising, it must be emphasised that the semiempirical methods developed at present for the numerical calculations of molecular force constants are extremely laborious and are applied mainly to diatomic molecules; moreover, the spectroscopic constants obtained by such calculations are still much inferior in their accuracy to the experimental constants, but the trend towards a reduction of errors in the calculations is quite definite.

III. ANALYTICAL METHODS FOR THE CALCULATION OF FORCE CONSTANTS

The analytical methods for the determination of force constants include the following: (1) analytical differentiation of the expression for the energy of the system obtained by a quantum-mechanical method; (2) the use of the differential Hellmann–Feynman theorem; (3) the use of the quantum-mechanical virial theorem; (4) the application of perturbation theory and various semiempirical variation-perturbation schemes.

Calculations of the harmonic force constants for a number of diatomic and polyatomic molecules based on the first procedure were made largely by Bratož and coworkers and also by Bishop and coworkers using both one-centre functions and Hartree–Fock–Roothaan functions in the self-consistent field approximation.

Thus the force constants of the molecules H_2 and LiH were calculated[40,50] from theoretical expressions obtained by Bratož[51] for the first and second derivatives of the total energy with respect to a parameter in terms of the LCAO-MO-SCF approximation and taking into account the configuration interaction[29]. It has been found that, when the method under consideration is employed, the molecular force constants agree better with experiment in the Fock–Roothaan one-determinant approximation than when limited allowance is made for configuration interaction, although the latter does in fact lead to a correct dissociation limit but not always to the best values of the force constants (Fig. 3). In other words, we encounter here an example illustrating the known fact that[25] an approximate wave function giving the best value of the operator for one physical quantity is not necessarily satisfactory for the calculation of the expected value of the operator for another physical quantity. In our case this means that the usual quantum-chemical variational solutions are more sensitive to the position of the limit (the value of the energy) than to the form of the potential surface (the force constants).

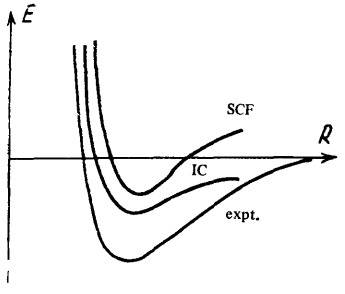


Figure 3.

Later it was shown[40] that, when the energy of the molecule is subdivided into the component E_n due to the interaction between the nuclei and the electrons of the skeleton and E_V due to the contributions of the electrons in the valence orbitals (such subdivision is always possible both in the self-consistent field method and in the method allowing for configuration interaction when in the latter case no account is taken of the excitation of the electrons of the skeleton), i.e.

$$E = E_n + E_v , \tag{10}$$

double differentiation yields

$$K_{\alpha\beta} = K_n + K_v . \tag{11}$$

It is found that $K_n \gg K_V$ for the force constants in the majority of diatomic molecules with a single bond (Table 1) and also for the diagonal force constants of molecules such as H_2O (Tables 2 and 3) and CH_4; this condition makes it possible to write

$$K_{\alpha\beta} \simeq K_n \simeq \frac{2}{R^3} . \tag{12}$$

Thus the main contribution to the force constants of the molecules considered is due to the interaction between the nuclei and the electrons of the skeleton. If the bond is not of a two-electron type, the results are less simple and Eqn. (12) no longer holds.

Bratož and coworkers arrived at a similar conclusion in their investigation [52,53] based on the one-centre model both in the one-determinant approximation and with allowance for configuration interaction, which is fairly acceptable, particularly within the framework of the analytical method for the differentiation of the energy of the system. Functions of this type describe satisfactorily the structure of hydrides the electrons of which are concentrated largely on one of the atoms and permit analytical differentiation of the matrix elements without additional limitations. It should be noted that, in contrast to such functions, the LCAO-MO-SCF functions require in their analytical evaluation on the basis of force constants the calculation of derivatives of many-centre integrals and also derivatives of orbital coefficients with respect to parameters. In view of the considerable difficulities in the solution of these problems, such calculations of the force constants are made largely on the basis of the simple wave functions of the molecular orbital and valence bond types (see below) and also the one-centre functions indicated above.

Table 2. The force constants of the water molecule (10^5 dyn cm^{-1}).

Force constant	K_n	K_v	$K_{\alpha\beta}$	Boys' data	Expt. (Ref.38)
$K_{\varphi\varphi}$	0.88	−0.01	0.87	0.86	0.77
$K_{R\varphi}$	0.31	0.05	0.36	−0.36	0.25
$K_{RR'}$	1.04	−1.11	−0.07	−0.62	−0.11

Thus, in terms of the one-centre approximation, it is easy to obtain [51,52] general formulae for the first, second, etc. derivatives of the energy of the ith state with respect to the nuclear coordinates, for example:

$$E_i^x = \sum_{s,t} d_{is}\, d_{it}\, H_{st}^x - \sum_{\alpha>\beta} Z_\alpha Z_\beta \frac{R_{\alpha\beta}^x}{R_{\alpha\beta}^2}, \qquad (13)$$

$$E_i^{xy} = \sum_{s,t} d_{is}\, d_{it}\, H_{st}^{xy} + \sum_{k}{}' [2/(E_i - E_k)] \times$$

$$\times \left(\sum_{s,t} d_{is}\, d_{kt}\, H_{st}^x\right)\left(\sum_{s,t} d_{is}\, d_{kt}\, H_{st}^y\right) + \sum_{\alpha>\beta} Z_\alpha Z_\beta (2R_{\alpha\beta}^x R_{\alpha\beta}^y - R_{\alpha\beta} R_{\alpha\beta}^{xy})/R_{\alpha\beta}^3, \qquad (14)$$

where d_{is} are the coefficients of the expansion in the wave function with configuration interaction in terms of the wave functions Φ_s of the united atom; H_{st}^x, H_{st}^y, and H_{st}^{xy} are the first and second derivatives with respect to the nuclear coordinates of the matrix element $H_{st} = \langle \Phi_s, H\Phi_t \rangle$. We may note that in the derivation of Eqns. (13) and (14) no approximation was made, since they are the true derivatives of the total energy for the given wave function with configuration interaction. The formulae will be particularly simple if it is postulated that the non-diagonal matrix elements are of the order of λ relative to the diagonal terms.

The calculation of the harmonic force constants with the aid of the one-determinant wave functions of the ground state, which is centrally-symmetrical, neglecting the second-order term [the first term is retained in Eqn. (14)], corresponds to Platt's electrostatic approximation‡, [54] i.e. to the hypothesis of a rigid electronic skeleton.

The application of the second order theory, i.e. the theory taking into account the second term in Eqn. (14), to calculations on polyatomic hydrides permits a detailed analysis of the various factors influencing the harmonic force constants of the molecules. This was done in the work of Bratož, Daudel, and others [52,53] for the H_2O and NH_3 molecules, the results of the calculations being compared, for water molecules, with the results of Boys [31], and also with experiment (Table 2).

Table 3. Force constants of the ammonia molecule (10^5 dyn cm^{-1}).

Force constant	1	2	3	$K_{\alpha\beta}$	Expt. (Ref.56)
K_{RR}	0.49	1.33	−1.79	9.03	1.17
$K_{RR'}$	0.88	0	−1.09	−0.21	0.08
$K_{\varphi\varphi}$	0.72	0.58	−0.44	0.86	0.91
$K_{R\varphi}$	0.26	0.136	−0.17	0.45	0.44
$K_{R\varphi}$	0	−0.36	0.26	−0.10	0.29
$K_{\varphi\varphi}$	0	−0.20	0.17	−0.03	−0.09

The fact that nuclear terms again make the main contribution to K_{RR} and $K_{\varphi\varphi}$ (as shown in Table 2) was demonstrated also in earlier studies by Longuet-Higgins and Brown [55] where the Platt model was applied to the polyatomic hydrides MH_n for the calculation of the stretching vibration frequencies on the basis of the electrostatic theorem.

Table 3, which gives the results of the calculation of various types of contributions to the harmonic force constants of the ammonia molecule, is also of interest. The first column corresponds to Platt's electrostatic approximation, which also makes the main contribution to the force constants K_{RR} and $K_{\varphi\varphi}$. When the wave function with configuration interaction, is employed, the contribution due to the introduction of additional configurations, neglecting the second term in Eqn. (14), is given in the second column; the electronic skeleton remains rigid as before ($d_{is}^x = 0$)—this is the so called "deformation" contribution. Finally, the third column lists the contributions due to the change in the wave function during vibrations, which is taken into account by the second term in Eqn. (14)—the "relaxation" contribution. The relaxation-deformation contributions play an appreciable role in non-diagonal force constants, particularly in $K_{R\varphi'}$ and $K_{\varphi\varphi'}$.

Thus the theory developed by Bratož and coworkers does not postulate that the wave function is spherical and that the electronic distribution is rigid [a rigid distribution is partly attained by taking into account the variation of the

‡We may note that Platt's model, which is based on two hypotheses (that the interatomic distance is close to $R_{1.0}$, the radius of the united atom in which the effective charge is unity, and that the force constant is approximately $4\pi\rho_{1.0}$, where $\rho_{1.0}$ is the electron density for the united atom at radius $R_{1.0}$), gives a satisfactory representation and prediction of the harmonic force constants for hydrides of the type AH.

linear coefficients d_{is} in the wave functions with the nuclear coordinates, which is in fact the reason for the appearance of the second term in Eqn. (14)].

It should be noted that Bishop and coworkers [33-35,37,39,57] carried out one-centre calculations of the force constants of a number of di- and poly-atomic hydrides (LiH, BeH, CH, BH, NH, OH, NH_3, H_2O, CH_4, and others), in different versions, corresponding to the removal of one or other limitation.

In a recent study by Bishop and Randic [38] the variation of non-linear parameters (orbital exponents) with the nuclear coordinates was included analytically in the expressions for the (harmonic) force constants of the H_2O molecule within the framework of the one-centre one-determinant wave function quoted by Allavena and Bratož. [33] The values of the force constants obtained here agree better with experiment than those calculated with the same accuracy but without taking into account the above relation (the agreement is better not only in magnitude but also in sign). In the same study the possibility of applying the authors' approach to one-centre functions, including configuration interaction, is also discussed.

Summarising, we may note that there is no doubt about the usefulness of further study of the functions under discussion, particularly for the calculation of anharmonic molecular force constants.

We shall consider further the possibilities of the differential Hellmann–Feynman theorem [58-60] and the quantum-mechanical virial theorem [61,62], which has recently found some application in the consideration of molecular forces [63-65] and force constants, mainly for diatomic molecules. The respective expressions for the theorems can be written as follows:

$$\frac{\partial E}{\partial x_\alpha} = \langle \Psi, \partial H/\partial x_\alpha \Psi \rangle, \tag{15}$$

$$\langle \Psi, T\Psi \rangle + E + \sum_{\alpha=1}^{N} X_\alpha \frac{\partial E}{\partial X_\alpha} = 0, \tag{16}$$

where, as usual, Ψ is the wave function for the system of $X_\alpha - 3N$ Cartesian coordinates (x_α, y_α, z_α) of N nuclei. It is seen from Eqns. (15) and (16) that the theorems yield the first derivative of the energy as the usual, expectation value of the corresponding operator, which permits $n - 1$ differentiations in order to obtain the nth derivative of the energy. As shown for the first time by Brown [66], the expressions for the harmonic force constants obtained by the differentiation of the Hellmann–Feynman theorem contain the integral of the derivative of the square of the modulus of the electronic wave function of the ground state with respect to a parameter (the internuclear distance in diatomic molecules).

Differentiation of the virial theorem for a diatomic molecule gives

$$K_{\alpha\beta} = \frac{1}{R_e}\left(\frac{\partial}{\partial R}\langle \Psi, V\Psi \rangle\right)_e, \tag{17}$$

or

$$K_{\alpha\beta} = -\frac{1}{R_e}\left(\frac{\partial}{\partial R}\langle \Psi, T\Psi \rangle\right)_e \tag{18}$$

Clinton [67] also concluded that the change in electron density cannot be ignored, since it is responsible for a non-vanishing contribution to the force constant. From this standpoint, he considered Platt's model, which remains attractive from the computational point of view, at least for diatomic hydrides, but is nevertheless purely formal.

Differentiation of the Hellmann–Feynman theorem makes it possible to express the force constant in the form [41]

$$K_{\alpha\beta} = Z_\alpha\left[Q_\alpha + \tfrac{4}{3}\pi\rho(\alpha) - \int \frac{\partial \rho}{\partial x_\alpha}\frac{\cos\theta_\alpha}{r_\alpha^2}\,d\tau\right]_e, \tag{19}$$

where Q_α is the electron density gradient at the nucleus α due to all the charges outside the limit of the nuclear radius (this term enters into the nuclear quadrupole coupling constant and may be obtained experimentally from the hyperfine structure of the rotational spectra [68] and $\rho(\alpha)$ is the charge density at the nucleus α. With regard to the last term in Eqn. (19), it can be shown, using either Eqn. (20), [96]

$$\frac{\partial \Psi}{\partial x_\alpha} = -\sum_n{}' \frac{(\partial H/\partial x_\alpha)_{0n}}{E_n - E_0}\cdot \Psi_n, \tag{20}$$

or the quantum-mechanical sum rule [42], that

$$-Z_\alpha \int \frac{\partial \rho}{\partial x_\alpha}\cdot\frac{\cos\theta_\alpha}{r_\alpha^2}\,d\tau = -2\sum_n{}' \frac{|(\partial V/\partial x_\alpha)|_{0n}^2}{E_n - E_0}, \tag{21}$$

the physical significance of which will be elucidated below. We may note that Eqn. (19) makes it possible to establish a relation between the force constant and the nuclear quadrupole coupling constant in a diatomic molecule, which is of considerable interest for theoretical chemistry.

Using the Hellmann–Feynman theorem, Salem [42] obtained second- and third-order force constants for the molecules H_2, Li_2, Na_2, and F_2 and also the force constants and the quadrupole coupling constants for diatomic hydrides from simple wave functions of the molecular orbital and valence bond type; on the basis of the properties of the electron density of the hydrides, it was shown that, for ionic hydrides of the type M^+H^-, Eqn. (19) becomes particularly simple and the force constants of these molecules can be expressed directly in terms of the quadrupole coupling constant:

$$K_{\alpha\beta} \simeq Q_H \simeq \frac{2}{R^3}.$$

Further mathematical forms which the force constants for di- and poly-atomic molecules can assume were investigated by Phillipson [43,69], who showed that the form of the equations depends on whether the virial or the Hellmann–Feynman theorem is employed and also on the coordinate system used to describe the wave functions.

Phillipson also studied the problem of the so called "stable" [70] functions, i.e. the approximate wave functions satisfying theorem (15). In the expressions which he obtained for the force constant account is taken of the dependence on internuclear distance of the parameters entering into the wave function:

$$K_{\alpha\beta} = \frac{1}{R_e}\left[\sum_i \left(\frac{\partial \bar{V}}{\partial \lambda_i}\right)\frac{d\lambda_i}{dR} - \frac{\bar{V}}{R^2}\right]_e, \tag{22}$$

$$\bar{V} = \langle \Psi(\lambda), V\Psi(\lambda)\rangle.$$

$$K_{\alpha\beta} = \left[-\sum_i (\partial \bar{F}/\partial\lambda_i)\frac{d\lambda_i}{dR}\right]_e,$$

$$\bar{F} = -\left\langle \Psi(\lambda), \frac{\partial V}{\partial R}\Psi(\lambda)\right\rangle, \tag{23}$$

where the summation is carried out with respect to all the variational parameters λ_i entering into the function Ψ. We may note that Eqn. (22) was obtained by differentiating Eqn. (16) on the assumption that the variational principle is satisfied, i.e. $dE/d\lambda_i = 0$, and Eqn. (23) was derived from Eqn. (15) on the assumption that the variational principle, the virial theorem, and the Hellmann–Feynman theorem are satisfied for all R.

Using simple wave functions of the molecular orbital and valence bond type, the force constants for H_2^+ and H_2 molecules were subsequently calculated [44] on the basis of Eqns. (23). Best agreement with experiment is achieved when Eqn. (22) is used, since none of the functions investigated satisfy theorem (15). The calculation suggests that, in order to obtain force constants comparable with the experimental values, it is necessary to have functions which describe accurately the curvature of the potential curve near R_e and satisfy the condition of zero force at the equilibrium point.

In a study by the present authors [47] which preceded those of Phillipson [43,44,59], the quadratic and cubic force constants of the H_2 and Li_2 molecules were calculated using relations of type (23) together with an investigation of the possibility of using the atomic wave functions with an angular variation of the effective charge to construct molecular wave functions satisfying the Hellmann–Feynman theorem. It was also shown that, when the condition $F_{Re} = 0$ is satisfied and a reasonable relation between the parameters (for example the orbital exponents in atomic orbitals) and the internuclear distance is introduced leading to the accurate curvature of the potential curve, satisfactory agreement with experiment is obtained for both the force constants and the binding energy (Table 1), although the latter, as already pointed out, is not necessarily a criterion of the derivation of satisfactory force constants.

Benston and Kirtman [45] continued the studies of the various forms which the second- and third-order force constants of diatomic molecules can assume depending on which coordinates are chosen for the description of electronic motion; they calculated the force constants of H_2 molecules on the basis of functions of the same type (molecular orbital and valence bond). One can say (Table 1) that the force constants may be calculated with adequate accuracy with the aid of both theorems provided that scaled functions, i.e. functions for which the orbital exponents in the atomic orbitals are optimised for all R, are employed.

In a study by the present authors [23,48,49], a new method was developed for the calculation of force constants. It was shown that in the Hartree–Fock–Roothaan self-consistent field approximation it is possible to take into account the variation of the Fock–Dirac density matrix with parameters which depend on the coordinates of the nuclei. However, numerical evaluation of the latter expressions for the nth order derivatives with respect to parameters is associated with a fairly large volume of calculations, mainly the need to calculate the derivatives of two-electron many-centred integrals. The use of the virial theorems (15) and (16) made it possible to represent the force constants in terms of derivatives of the matrix elements of one-electron operators and thus avoid the above difficulty. We shall now quote formulae for the second- and third-order derivatives obtained by direct differentiation of the virial theorem formulated in terms of the LCAO-SCF procedure for diatomic molecules (in terms of a system of electronic coordinates linked with the centre of gravity of the molecule):[23]

$$K_{\alpha\beta} = -\frac{2}{R_e} Sp\left[\rho\frac{\partial T}{\partial R} - \rho(aT + \tilde{Ta})\right]_e,$$

$$K_{\alpha\beta\gamma} = -\frac{3}{R_e}K_{\alpha\beta} - \frac{2}{R_e} Sp\left[\rho\frac{\partial P}{\partial R} - \rho(aP + \tilde{Pa})\right]_e,$$

where $P = \partial T/\partial R - (aT + \tilde{Ta})$, $\rho = C\tilde{C}$, $a = \mu S^{-1}$ and μ is a matrix with the elements $\mu pq = <\partial\chi p/\partial R, \chi q>$.

Specific calculations of the force constants (up to the fourth order inclusive) performed on the basis of one-determinant Hartree–Fock–Roothaan functions for a number of diatomic hydrides and the water molecule [23,71] suggest that the method developed is applicable to the calculation of the potential functions for small molecules.

It is necessary to emphasise the importance of the condition that the approximate wave function employed should satisfy the virial and Hellmann–Feynman theorems if acceptable force constants are to be obtained (Table 1). Moreover, if one ensures that the Hartree–Fock function with a limiting-basis set is close to the true Hartree–Fock function, one may expect a second-order perturbation error in the calculation of the expected value of the one-electron operator [72].

The possibility of deriving theoretical expressions for derivatives higher than second order for the energy of diatomic molecules on the basis of theorems (15) and (16) has been demonstrated recently by Schwendeman [73]. The expressions obtained make it possible to establish rigorous relations between the experimental spectroscopic constants and derivatives of the kinetic and potential energies and hence permit assessment of the suitability of the quantum-mechanical calculations of the latter based on a particular approximate function. The same investigator [53] has carried out such an analysis for carbon monoxide; it consists in the following steps: the values of the total kinetic and potential energies found by Hartree–Fock calculations [11] were used to obtain by a numerical method the derivatives of these quantities with respect to R. These values are compared with those calculated with the aid of the relations indicated above. Thus it is possible to investigate the suitability of particular approximate Hartree–Fock functions for the calculation of force constants on the basis of the virial theorem. In this work on the carbon monoxide molecule, the satisfactory agreement of the calculated derivatives of T, V, and E suggests that there is no doubt that Hartree–Fock functions can be used in thise case. We may also note that, when scaled wave functions are employed, it is possible to achieve a more flexible R-behaviour of the potential curve [45,74].

We shall consider further a method based on the expansion of the electronic Hamiltonian in terms of powers of the displacement of the nuclei from the equilibrium positions with subsequent application of perturbation theory. The method was proposed by Brown [66], and has been developed and employed in a number of studies by Salem, Murrell, Bader, and others [41,42,75,76].

With the aid of second-order perturbation theory, the following expression was obtained for the harmonic force constant in the ground state:

$$K_{\alpha\beta} = \left[\left(\frac{\partial^2 H}{\partial R^2}\right)_{00} - 2\sum_n{}' \frac{|(\partial H/\partial R)_{0n}|^2}{E_n - E_0}\right]_e, \qquad (24)$$

which allows a physical interpretation of the following type: the first term is the average value of the operator d^2H/dR^2 at equilibrium and the second negative term reflects the variation of the force constant with the change in charge distribution caused by a change in the configuration of the molecule.

We must emphasise that the principal disadvantage of this approach and, incidentally, of any other where it is necessary to employ expansion (20) is the need to take into account the wave functions and energies of excited states, which are generally speaking unknown and, moreover, it is necessary to estimate the contributions from continuous energy states.

To eliminate this disadvantage, Benston and Kirtman [46] proposed another procedure [20] for finding the derivatives of the approximate wave functions. According to perturbation theory, the second- and third-order force constants for a diatomic molecule are expressed in terms of Ψ_0 and Ψ_1 respectively and the unperturbed and first-order wave functions. In turn $d\Psi/dR$ corresponds to the function Ψ_1, i.e. the problem reduces to finding Ψ_1. This is done by the variational method (the first attempt was made by Mills [77] for the CH_4 molecule). The formulae expressing $K_{\alpha\beta}$ and $K_{\alpha\beta\gamma}$ in terms of Ψ_0 and Ψ_1, found from the variational principle, are of the form

$$K_{\alpha\beta} \simeq \langle \Psi_0, H_2\Psi_0\rangle + 2\langle \Psi_1^{opt}, (H_0 - E_0)\Psi_0\rangle,$$

$$K_{\alpha\beta\gamma} \simeq \langle \Psi_0, H_3\Psi_0\rangle + 6\langle \Psi_1^{opt}, (H_2 - E_2)\Psi_0\rangle + 6\langle \Psi_1^{opt}, (H_1 - E_1)\Psi_1^{opt}\rangle, \quad (25)$$

where

$$H_n = \left(\frac{\partial^n H}{\partial R^n}\right)_e;$$

the expressions for E_n and Ψ_n are analogous.

For the H_2 molecule discussed by Benston and Kirtman [46], Ψ_1 was approximated by a linear combination of derivatives of the covalent and ionic functions from which Ψ_0 was derived.

The coefficients in the expression for Ψ_1 are then determined from the condition for an energy minimum in the second approximation. The results of the calculations agree well with experiment; for example, the Weinbaum function gives $K_{\alpha\beta} = 0.362$ a.u. and $K_{\alpha\beta\gamma} = -1.43$ a.u., while the experimental values are $K_{\alpha\beta} = 0.368$ a.u. and $K_{\alpha\beta\gamma} = -1.30$ a.u.

In general the different forms of Eqn. (24) obtained depending on the coordinate system chosen for the wave function are not readily susceptible to a quantitative analysis but they may be useful (as well as the expressions obtained from the analytical methods discussed above) for the understanding of the nature of the intramolecular forces. For example, Bader [76] employed such expressions for a qualitative physical interpretation of non-diagonal bond-interaction force constants in the potential function for polyatomic molecules (linear and non-linear triatomic and also pyramidal and planar tetra-atomic molecules), in particular in order to predict their magnitude and sign. It was found that both the magnitude and the sign of such constants are determined largely by the second term in Eqn. (24). It has been shown [75] for diatomic molecules that the first term of Eqn. (24) is largely responsible for the variation of $K_{\alpha\beta}$ in a series of isoelectronic molecules and the second changes steadily from one group of elements with identical nuclei to another, which permits the prediction of the direction of change in the force constant and is fully consistent with the above physical interpretation of the terms of Eqn. (24). Attention should be drawn to the fact that unfortunately very few studies dealing with the solution of this problem have been published in the Soviet literature.

One of the first studies on the application of analytical methods is that of Kovner and Tsimring [78] dealing with the determination of the harmonic force constants of the methane molecule. The idea of the one-centre approximation found an interesting development in investigations carried out in Veselov's laboratory. Thus, using the LCAO-MO method on the basis of a two-centre basis set, Bulychev [79] obtained the force constant for the stretching of the C ≡ C bond in acetylene, in good agreement with experiment; we believe that the force constant for the stretching of the C–H bond calculated by Bulychev is in good qualitative agreement with experiment and evidently the agreement can be improved by extending the basis set.

Adamov and Bulychev [80] carried out an improved calculation of the total energy of the H_2 molecule on the basis of the Weinbaum function corresponding to the superposition of covalent and ionic states; their analysis [80] of the potential curve made it possible to obtain spectroscopic constants in satisfactory agreement with the available data.

In conclusion we wish to express the hope that in the near future the above gap will be filled and that the numerical and analytical methods described here will permit the determination of the relative and absolute values of the potential constants, which will undoubtedly prove useful for the understanding of the nature of the forces between atoms in the molecule and also for the solution of spectrochemical problems.

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