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Some Recent Results concerning the Electronic Density and the Force Constants of Small Molecules

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SOME work has recently been done in this Laboratory in order to get new information on the nature of the chemical bonds of small molecules. Two topics have been selected for this discussion: (1) the effect of binding on electronic density of small molecules; (2) the force constants of some simple hydrides.

EFFECT OF BINDING ON ELECTRONIC DENSITY OF SMALL MOLECULES

A chemical bond has been characterized[1] by means of the function $\delta(\mathbf{R})$ defined as

$$\delta(\mathbf{R})=\rho(\mathbf{R})-\rho^F(\mathbf{R}). \qquad (1)$$

$\rho(\mathbf{R})$ is the electronic density at a point $\mathbf{R}$, and $\rho^F(\mathbf{R})$ that which would result if two atoms making up the molecule could be added together without perturbing each other. The function $\delta(\mathbf{R})$ is a measure of the distortion of the atomic electronic clouds subsequent to the bond formation. In a region where $\delta(\mathbf{R})$ is positive, there is an accumulation of electrons while the opposite is true where $\delta(\mathbf{R})$ is negative. A number of molecules for which good wave functions are available were analyzed by this method.

(1) H_2 Molecule

James and Coolidge's wave function[2] was used for this molecule. In this case δ was found to be positive along the line joining the two H atoms as shown in Fig. 1. This agrees well with the Lewis notation for a single covalent bond. In a bond of this type, there is an increase of the electronic density between the nuclei.[3]

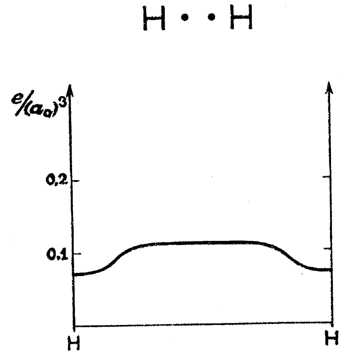

FIG. 1. The function $\delta(\mathbf{R})$ calculated for H_2 along the molecular axis. The corresponding Lewis formula is added.

(2) N_2 Molecule

Scherr's SCF wave function[4] was used in this case, and δ was calculated on a plane passing through the two atoms. One finds (Fig. 2) that δ is negative along the molecular axis but positive in an annular region centered on the molecular axis and in regions appearing at each "end" of the molecule. The triple bond in N_2 is therefore annular in some sense. The presence of the "end" regions is probably due to the existence of unshared pairs of electrons. Finally, the description of the bond in N_2, given by $\delta(\mathbf{R})$ is in fair correlation with the usual Lewis formula of N_2 (Fig. 2).

(3) O_2 Molecule

The wave function based on a configuration interaction with five terms obtained by Kotani and his colleagues[5] has been used in calculating ρ, ρ^F, and δ for this system. All these quantities were calculated in a plane passing through the molecular axis. There is a difficulty concerning the definition of the δ function in this case; the electronic density of the free oxygen atom[6] is not spherical and it is not very clear how to form ρ^F. The definition has been adopted according to which ρ^F is to be formed with the help of atomic densities averaged over all orientations in the space; in this way, the spherical symmetry is reintroduced. As for N_2, no increase of electronic density is found along the molecular axis (Fig. 3). The O_2 bond is again of the annular type. However, the annular regions are placed in a different way. There are three in number: two at the "ends" of the molecule and one between them. The behavior at the "end" regions is probably due to the fact that on each oxygen atom there are four unshared electrons. This leads to a strong repulsion between the electrons of the same spin. Once more the results are in good qualitative agreement with the Lewis classical scheme (Fig. 3).

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[1] M. Roux, S. Besnainou, and R. Daudel, J. chim. phys. 218 (1956).

[2] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[3] Reference 1, p. 939.

[4] C. W. Scheer, J. Chem. Phys. **23**, 569 (1955).

[5] M. Kotani, Y. Mizuno, K. Kayama, and E. Ishiguro, J. Phys. Soc. Japan **12**, 707 (1957).

[6] The fundamental state of O is a $^3P_2$ state.

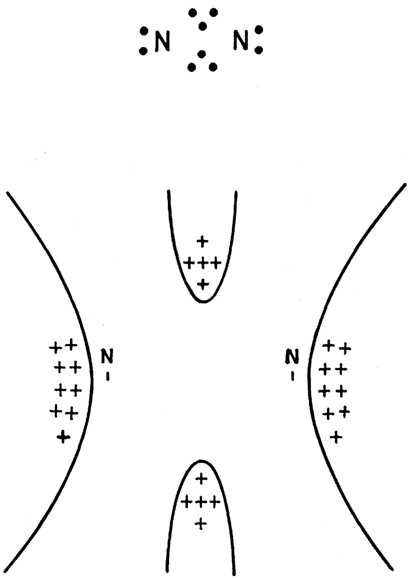

FIG. 2. The function $\delta(\mathbf{R})$ calculated for N_2 in a plane passing through the molecular axis. The regions where $\delta(\mathbf{R})$ is positive are designated by crosses. The corresponding Lewis formula is added.

Conclusion

The results obtained by use of elaborate wave functions agree qualitatively with what could be expected from simple chemical intuition. It is important, however, that this agreement is not quantitative: the charge localized in the annular region is much smaller than the classical formula suggests; in the annular region of N_2 the binding leads to an increase of no more than 0.01 electron. Recent experimental works on benzene lead to similar conclusions.[7]

FORCE CONSTANTS OF SOME SIMPLE HYDRIDES

It has been shown (Platt[8]) that the force constants of diatomic hydrides MH can be calculated surprisingly well by a simple model of the united-atom type. This section examines the following questions: (a) How can Platt's model be incorporated into the perturbation-theory scheme based on the united-atom orbitals? (b) What can such a theory say about the factors influencing the force constants of the diatomic molecules? (c) How can this method be extended to the case of polyatomic hydrides in order to investigate the bending and interaction force constants?

(1) General Theory

If the electrons of a diatomic or polyatomic molecule are strongly concentrated on one of the atoms (which is the case for hydrides) it is reasonable to develop the molecular wave function into a series of the united-atom wave functions. If ϕ_0, ϕ_1, etc. are the wave functions in the united atom, say in the SCF approximation, the molecular wave function ψ_i can be written

$$\psi_i=\sum_s d_{is}\phi_s, \tag{2}$$

where d_{is} are the expansion coefficients. The corresponding energy derivatives can be calculated.[9] The results are particularly simple if one introduces the usual hypothesis of the perturbation theory ($H_{ii}\rightarrow H_{ii}$, $H_{ik}\rightarrow \lambda H_{ik}$; $E_i\rightarrow E_i^0+\lambda E_i^1+\cdots$). This gives (see the Appendix)

$$\left.\begin{aligned}E_i^x&=H_{ii}^x+\lambda^2\left[2\sum_s{}'\frac{1}{H_{ii}-H_{ss}}H_{is}H_{is}^x\right.\\&\qquad\left.-\sum_s{}'\frac{H_{is}^2}{(H_{ii}-H_{ss})^2}(H_{ii}^x-H_{ss}^x)\right],\\E_i^{xy}&=H_{ii}^{xy}+\lambda^2\left[2\sum_s{}'\frac{1}{H_{ii}-H_{ss}}(H_{is}H_{is}^{xy}+H_{is}^xH_{is}^y)\right.\\&\qquad\left.-\sum_s{}'\frac{H_{is}^2}{(H_{ii}-H_{ss})^2}(H_{ii}^{xy}-H_{ss}^{xy})\right].\end{aligned}\right\} \tag{3}$$

In these formulas $E_i^x=\partial E/\partial S_x$ and $E_i^{xy}=\partial^2E/\partial S_x\partial S_y$ are the derivatives of the energy of the molecular electronic state i (ground state) with respect to S_x and S_y; S_x and S_y are the nuclear coordinates, by preference the

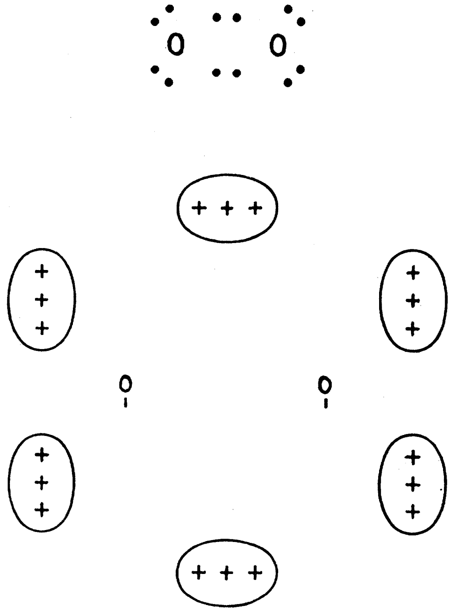

FIG. 3. The function $\delta(\mathbf{R})$ calculated for O_2 in a plane passing through the molecular axis. The regions where $\delta(\mathbf{R})$ is positive are designated by crosses. The corresponding Lewis formula is added.

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[7] W. Cochran, Acta Cryst. 9, 924 (1956).

[8] J. R. Platt, J. Chem. Phys. 18, 932 (1950).

[9] S. Bratož, *Calcul des Fonctions d'onde Moleculaires* (Colloques internationaux du CNRS, Paris, 1958), p. 287.

symmetry coordinates.[10] H_{is} is the matrix element $\langle\phi_i|H|\phi_s\rangle$ and H is the total molecular Hamiltonian; $H_{is}{}^x$ and $H_{is}{}^{xy}$ are the corresponding derivatives

$$H_{is}{}^x=(\partial/\partial S_x)\langle\phi_i|H|\phi_s\rangle,\quad H_{is}{}^{xy}=(\partial/\partial S_x\partial S_y)\langle\phi_i|H|\phi_s\rangle.$$

The force E^x as well as the force constant E^{xy} are composed as expected of a zero-order term associated with the diagonal matrix elements $H_{ii}{}^x$ and $H_{ii}{}^{xy}$ as well as of second-order terms associated with nondiagonal elements. Here it is convenient to separate the discussion into the sections dealing, respectively, with the diatomic and polyatomic molecules.

(2) Diatomic Hydrides MH—Formal Derivation of Platt's Formula

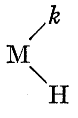
If one neglects the second-order terms, Eqs. (3) reduce to the form

$$dE_1/dS_x=-F=dH_{11}/dS_x;\quad d^2E_1/dS_x{}^2=d^2H_{11}/dS_x{}^2,\quad (4)$$

where we have put $i=1$. This approximation corresponds to Platt's theory. This can be easily proved if one considers the atom M as fixed in space; the position of the H with respect to M is described by the coordinate $S_x=R$, the distance between M and H. The atomic wave functions centered on the fixed atom M do not depend on R; neither do the kinetic energy and the electronic repulsion operators. The force acting on the H nucleus is then

$$-F=\frac{dH_{11}}{dR}=\frac{d}{dR}\langle\phi_1|H|\phi_1\rangle=\left\langle\phi_1\left|\sum_k\frac{\cos\theta_k}{r_{k\mathrm{H}}{}^2}\right|\phi_1\right\rangle-\frac{Z_{\mathrm{M}}}{R^2}$$
$$=\int\rho\frac{\cos\theta}{r_{\mathrm{H}}{}^2}dv-\frac{Z_{\mathrm{M}}}{R^2};\quad (5)$$

$r_{k\mathrm{H}}$ is the distance between the electron k and the proton, θ_k is the angle



and ρ the electronic density; F can be evaluated easily if one supposes that the charge distribution is spherical.[11] With the help of a well-known theorem of classical electrostatics, one finds

$$-F=(1/R^2)\int_0^R 4\pi r^2\rho dr-(Z_{\mathrm{M}}/R^2)$$
$$=(1/R^2)\left(\int_0^R 4\pi r^2\rho dr-Z_{\mathrm{M}}\right).\quad (6)$$

For the equilibrium distance $F=0$ or

$$\int_0^R 4\pi r^2\rho dr=Z_{\mathrm{M}}.\quad (7)$$

The integral $\int_0{}^R 4\pi r^2\rho dr$ gives the number of electrons contained in a sphere with radius R centered on the united atom. Equation (7) then indicates that the equilibrium R is the radius in the united atom at which the effective nuclear charge is unity. This is the radius beyond which lie a total number of 1.0 electron. This is just the first Platt hypothesis. If one differentiates Eq. (6) with respect to R, one finds

$$(-dF/dR)=4\pi\rho-(2/R^3)\left(\int_0^R 4\pi r^2\rho dr-Z_{\mathrm{M}}\right).\quad (8)$$

The force constant is then

$$K=4\pi\rho,\quad (9)$$

which is the second Platt hypothesis. It is therefore shown that (1) the Platt model corresponds to the leading term of the perturbation development based on the united-atom wave functions; (2) Platt's formula is obtained only for a spherical charge distribution. On the contrary, the independence of the atomic wave function on R is not essential. Platt's formulas also could be obtained with atomic functions containing parameters which depend on R (e.g., orbital coefficients), provided they have been chosen in a way which satisfies the variation principle.[12] It should be stressed, however, that this formal justification of the Platt theory does not completely explain its success. It is not clear, for example, why the experimental and not the theoretical R must be used to get agreement with experience. An analysis of the higher-order terms would be necessary to clarify this point.

(3) Diatomic Hydrides—Study of Factors Influencing the Force Constants

In this section we examine how the electrons of different orbitals influence the force constant. It is convenient to start from the fact that in the single determinant approximation, the electronic density is composed additively of contributions associated with different orbitals. One has

$$\rho=2\rho_{1s}+2\rho_{2s}+\cdots.\quad (10)$$

The force with which the electrons attract the proton can be decomposed correspondingly:

$$-F^{\mathrm{el}}=\int\rho dv/R^2=2\int\rho_{1s}dv/R^2+2\int\rho_{2s}dv+\cdots$$
$$=-2F_{1s}{}^{\mathrm{el}}-2F_{2s}{}^{\mathrm{el}}-\cdots.\quad (11)$$

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[10] This choice of the nuclear coordinates conserves the usual symmetry arguments in calculating the matrix elements.

[11] The atomic charge distribution is spherical only for S states.

[12] A. C. Hurley, Proc. Roy. Soc. (London) **A226**, 173 (1957).

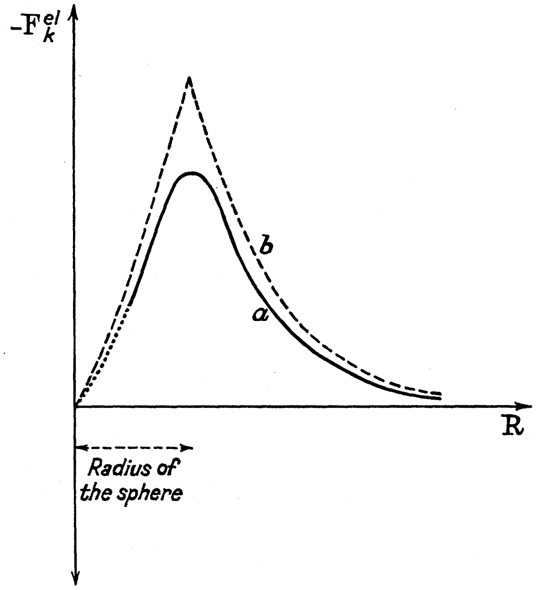

FIG. 4. The force F_k^{el} with which the charge associated with an orbital k attracts the proton, as a function of R: curve a, united-atom model; curve b, uniformly charged sphere approximation.

It is now stated that $F_k^{\mathrm{el}}=0$ for $R=0$ and $R=\infty$. For $R=0$ this is due to the fact that in the united-atom situation there is a center of symmetry. For $R=\infty$ one has $-F_k^{\mathrm{el}}\approx 1/R^2$, which proves the statement. As the forces F_k^{el} are attractive, hence negative, $-F_k^{\mathrm{el}}$ has (at least) one maximum (Fig. 4, curve a). The corresponding contributions to the force constant $d^2E_k^{\mathrm{el}}/dR^2$ are then obtained by differentiation (Fig. 5, curve a). $d^2E_k^{\mathrm{el}}/dR^2$ can be negative as well as positive; it is small in the neighborhood of the point where $-F_k^{\mathrm{el}}$ is maximum. An orbital whose attractive force is the largest possible does not contribute to the force constant. It can be shown that, in the uniformity charged-sphere approximation, the maximum binding force (or zero force-constant contribution) corresponds to the point where the proton begins to penetrate into the sphere (Figs. 4 and 5, curve b).

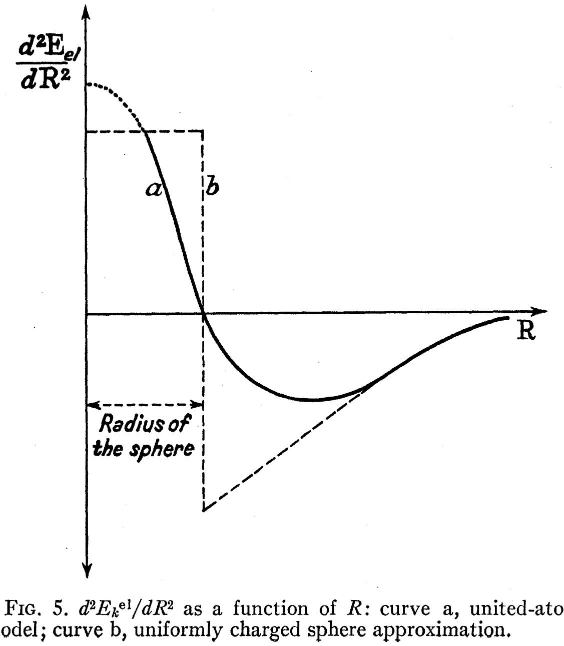

FIG. 5. $d^2E_k^{\mathrm{el}}/dR^2$ as a function of R: curve a, united-atom model; curve b, uniformly charged sphere approximation.

The way the electrons of different orbitals influence the force constants now can be readily explained. The core orbitals being "small" with respect to the M—H distance, one is on the right side of the curves of Fig. 5. Their contribution to the force constant is essentially $2/R^3$. The effect of the core orbitals is therefore to screen the nuclear charge of the atom M, which is an expected result. As the charge "dimensions" of the orbitals increase, one is shifting progressively to the left (Fig. 5). It follows that the bond orbitals contribute less to the force constants than do the core orbitals; their contribution to the force constants may become very small. Another way to express the same idea is to say that the bond orbital energy varies less rapidly in the neighborhood of the equilibrium R than does the core orbital energy; it may vary even in a quasi-linear fashion.[13] In some cases, these considerations lead to surprising results. If, e.g., for an essentially dielectronic bond, the valence orbital contribution to the force constant is small, it can be neglected and one has approximately $K=2/R^3$, i.e., the same result as if there were no valence electrons at all (Table I). If the bond is not essentially dielectronic, the results are less simple and the $2/R^3$ law is not expected to hold.

TABLE I.

Molecule	$2/R^3$ (10^5 dyne cm^{-1})	Exptl.	Molecule	$2/R^3$ (10^5 dyne cm^{-1})	Exptl.
LiH	1.14	1.01	CsH	0.30	0.47
BH	2.48	3.04	Li_2 [a]	0.24	0.25
NaH	0.68	0.78	Na_2 [a]	0.16	0.17
KH	0.41	0.56	K_2 [a]	0.08	0.10
RbH	0.37	0.51			

[a] The molecules Li_2, Na_2, and K_2 have been included although they are not hydrides.

The question could be raised as to whether the application of Platt's theory is justified in this connection. The answer is affirmative as the essential point, i.e., the fact that $d^2E_k^{\mathrm{el}}/dR^2$ vanishes for some R, is completely independent from Platt's hypothesis. It is simply a consequence of the fact that the electron-nuclei attractive forces have somewhere their maximum; in this point one has $-(dF/dR)=K=0$. A complete SCF-CI calculation on H_2 and LiH led to similar results.[14,15]

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[13] This has nothing to do with the stability of the molecule. Even a linear electronic potential would ensure the stability of the molecule although giving a zero contribution to the force constant.

[14] G. Bessis and S. Bratož, Compt. rend. 24, 1592 (1958).

[15] S. Bratož and G. Bessis, J. chim. phys. 1042 (1959).

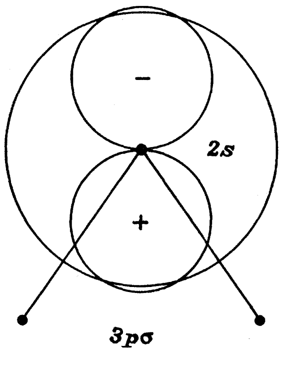


FIG. 6. The interaction of s and p wave functions introduces a density of p type.

(4) Polyatomic Hydrides—Force Constants of H_2O

The first-order theory, successful for diatomic hydrides, is clearly insufficient for the polyatomic hydrides. The reasons are: (1) The united atom associated, e.g., with H_2O is Ne. As its charge distribution is spherical, it cannot ensure the stability of a bent triatomic molecule such as H_2O. This can be made only if one allows the mixture of the fundamental S state with other states having symmetry P, D, etc. (Fig. 6). (2) It is impossible to get a nonvanishing electronic contribution to the interaction constants of stretching-stretching type if the wave function is not allowed to follow the nuclear motion. This is due to the fact that in the case considered, no molecular integral depends simultaneously on two different bond distances: $d^2E^{\mathrm{el}}/dRdR'$ is necessarily zero.

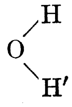
The constants K_α, $K_{R\alpha}$, and $K_{RR'}$ of H_2O are therefore studied by using the complete (second order) procedure (3). In this problem the O atom is considered as being fixed in space; the nuclear configuration is then completely described by three coordinates:

$$r_{\mathrm{OH}},\ r_{\mathrm{OH'}},\ \text{and}\ \alpha_{\mathrm{O}<^{\mathrm{H}}_{\mathrm{H'}}}.$$

Instead, the following symmetry coordinates will be used[16]:

$$S_x=2^{-\frac{1}{2}}(r_{\mathrm{OH}}+r_{\mathrm{OH'}});\quad S_y=\alpha_{\mathrm{O}<^{\mathrm{H}}_{\mathrm{H'}}};$$
$$S_z=2^{-\frac{1}{2}}(r_{\mathrm{OH}}-r_{\mathrm{OH'}}). \quad (12)$$

The OH distance has been taken equal to 0.97 A and



angle to 104° 30′. The atomic orbitals used are the orthogonalized Slater orbitals with the orbital coefficients taken from the work of Banyard and March[17]: $\zeta_{1s}=7.670$, $\zeta_{2s}=2.630$, $\zeta_{2p\sigma 1\pi}=1.885$.[18] For $3s,p$ orbitals the value $\zeta_{3s,p}=0.620$ has been chosen; this value is close to the value given by the Slater's rule when applied to the united atom (0.68). All integrals, including their derivatives, have been calculated analytically by using Kotani's and Roothaan's formulas.[19,20] The configurations of the states which have been included in the calculations are given in the Table II. All other configurations of the M shell have been found to give small contributions and have been neglected. The procedure has been simplified in one point, replacing the difference $H_{11}-H_{kk}$ by the calculated value of the first ionization potential of H_2O; this probably does not introduce serious errors as even the smallest $H_{11}-H_{kk}$ close to this value. The results are given in Table III, which also reproduces the results of Boys and colleagues[21] obtained by a complete SCF-CI calculation. As in the diatomic case, the agreement with experience is satisfactory if the experimental values are used for the internuclear distances.

TABLE III. (Calculations in 10^5 dyne cm^{-1}.)

	Boys and colleagues[a]	This work	Exptl.[b]
K_α	0.86	0.87	0.77
$K_{R\alpha}$	−0.35	0.36	0.25
$K_{RR'}$	−0.62	−0.07	−0.11

[a] See footnote 21.
[b] C. A. Coulson, J. Duchesne, and G. Manneback, *Volume Commemoratif Victor Henri* (Maison Desoer, Liège, Belgium, 1948), p. 33.

Some interesting conclusions can be drawn from this calculation. One observes, first of all, that the separation of the force constants K_α, $K_{R\alpha}$, and $K_{RR'}$ into zero- and second-order terms, coincides with the separation

TABLE II.

Configuration	Symmetry	Configuration	Symmetry
$(1s)^2(2s)^2(2p\sigma)^2(2p\pi)^2(2p\pi')^2$	A_1	$(1s)^2(2s)^2(2p\sigma)^2(2p\pi)^2(2p\pi')(3p\pi')$	A_1
$(1s)^2(2s)^2(2p\sigma)(2p\pi)^2(2p\pi')^2(3s)$	A_1	$(1s)^2(2s)^2(2p\sigma)(2p\pi)^2(2p\pi')^2(3p\pi)$	B_1
$(1s)^2(2s)^2(2p\sigma)(2p\pi)^2(2p\pi')^2(3p\sigma)$	A_1	$(1s)^2(2s)^2(2p\sigma)^2(2p\pi)(2p\pi')^2(3s)$	B_1
$(1s)^2(2s)^2(2p\sigma)^2(2p\pi)(2p\pi')^2(3p\pi)$	A_1	$(1s)^2(2s)^2(2p\sigma)^2(2p\pi)(2p\pi')^2(3p\sigma)$	B_1

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[16] Compare with footnote 10.
[17] K. E. Banyard and N. H. March, Acta crystal. **9**, 385 (1956).
[18] They have been determined minimizing the H_2O molecular energy.
[19] M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen Company, Ltd., Tokyo, 1955).
[20] C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).
[21] S. F. Boys, G. B. Cook, C. M. Reeves, and I. Shavtt, Nature **178**, 1207 (1956).

TABLE IV. (Calculations in 10^5 dyne cm^{-1}.)

	Nuclear contribution	Electronic contribution	Total
K_α	0.88	−0.01	0.87
$K_{R\alpha}$	0.31	0.05	0.36
$K_{RR'}$	1.04	−1.11	−0.07

into the nuclear repulsion and electron-attraction terms. One finds, in fact, that the nuclear terms are exceptionally large for K_α and $K_{R\alpha}$ [22] (Table IV). The result is unexpected but not entirely new. The fact that the bending frequency ν_2 of the tetrahedral hydrides MH_4 can be reproduced reasonably well by a formula depending only on R_{MH} (Longuet-Higgins and Brown[23]) is due to the same reason. The electronic correction is, on the contrary, important for the stretching-stretching interaction constant $K_{RR'}$ where it reverses the sign of the zero-order term. As the electronic term measures the electronic rearrangement during vibration, it follows that the negative sign of $K_{RR'}$ is due to the "electronic relaxation."[24] It seems that the matters are similar in the case of other hydrides. One finds that the nuclear repulsion terms reproduce well the constants K_α and $K_{R\alpha}$ but not $K_{RR'}$. However, the electron rearrangement contribution to $K_{RR'}$ is not necessarily larger than the nuclear term; these constants are therefore positive or negative, but small.

APPENDIX

For a configuration interaction wave function the derivatives of the energy E_i with respect to the nuclear coordinates S_x and S_y are given by the following formulas[9]:

$$E_i^x = \sum_{st} d_{is} d_{it} H_{st}^x, \qquad \text{(a)}$$

$$E_i^{xy} = \sum_{st} d_{is} d_{it} H_{st}^{xy} + \sum_k{}' \left[2/(E_i - E_k)\right] \times \left(\sum_{st} d_{is} d_{kt} H_{st}^x\right)\left(\sum_{st} d_{is} d_{kt} H_{st}^y\right). \qquad \text{(b)}$$

Here d_{is}, d_{it}, etc. are the expansion coefficients of the CI wave function ψ_i into (finite) sum of determinants ϕ_s; H_{st} are the matrix elements $\langle\phi_s|H|\phi_t\rangle$, H being the total molecular Hamiltonian. One also has

$$\begin{aligned} H_{st}^x &= (\partial/\partial S_k)\langle\phi_s|H|\phi_t\rangle; \\ H_{st}^{xy} &= \partial^2/\partial S_x \partial S_y \langle\phi_s|H|\phi_t\rangle; \qquad \text{(c)} \\ E^x &= \partial E/\partial S_x; \\ E^{xy} &= \partial^2 E/\partial S_x \partial S_y. \end{aligned}$$

For an exact wave function ψ_i, i.e., for a development which is not truncated, formula (b) coincides with one given by Brown.[25] Formulas (a) and (b) can be simplified considerably if one supposes that the nondiagonal matrix elements (as well as then derivatives) are of order λ with respect to the diagonal terms. By substituting λH_{ik} for $H_{ik}(i \neq k)$ into the system of the linear equations which determines the d_{is}, one gets the simplified expressions for the configuration interaction expansion coefficients:

$$d_{ii} = 1 - \lambda^2 \tfrac{1}{2} \sum_k{}' \left[H_{ik}^2/(H_{ii} - H_{kk})^2\right] + \cdots, \qquad \text{(d)}$$

$$d_{ik} = \lambda\left[H_{ik}/(H_{ii} - H_{kk})\right] + \cdots. \qquad \text{(e)}$$

Formulas (d) and (e) have a more similar structure than those given by the ordinary perturbation theory. Substituting (d) and (e) into (a) and (b), one obtains the formulas (3) of the text.

ACKNOWLEDGMENTS

The authors wish to thank Professor J. R. Platt and Professor J. Duchesne for a critical reading of the manuscript.

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[22] Compare with footnote 13.

[23] H. C. Longuet-Higgins and D. A. Brown, J. Org. Nuclear Chem. 1, 60 (1955).

[24] I. B. Mills, Mol. Phys. 1, 107 (1958).

[25] W. Byers Brown, Proc. Cambridge Phil. Soc. 57, 251 (1958).

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Quantum Mechanical Calculations of Short-Range Intermolecular Forces*

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BY short-range intermolecular forces we mean those forces whose potential energy is in the range of a few tenths of an electron volt to a few electron volts. Such forces are important in determining most properties at very high temperatures and a few properties at ordinary temperatures that are selective for high-energy molecular collisions. At present there is an especially great need for information on the transport properties

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