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Department of Mathematics, University of Nottingham, Nottingham

Isoelectronic sequences of hydride molecules

By

G. G. **Hall** and D. **Rees**

The theory of the electronic structure of diatomic hydrides in which the nuclear charge of the second nucleus is varied freely is investigated. By the use of a scale factor which varies with both the nuclear charge and the internuclear distance, the electronic equation can be put into a form suitable for a perturbation expansion. The zero and first order energies are computed for a number of isoelectronic sequences but comparisons with experiment show that higher order terms are needed in order to explain the basic properties of the molecules.

Die Theorie der Elektronenstruktur zweiatomiger Hydride wird untersucht, wobei die zweite Kernladungszahl frei veränderbar bleibt. Durch Einführung eines Maßstabfaktors, der sowohl von Kernladungszahl als auch zwischenatomarem Abstand abhängt, läßt sich die Schrödingergleichung in eine die Durchführung einer Störungsrechnung möglich machende Form bringen. Die Energien nullter und erster Näherung werden für eine Anzahl isoelektrischer Reihen berechnet, allein der Vergleich mit dem Experiment zeigt, daß Terme höherer Ordnung in die Rechnung mit einbezogen werden müssen, um Grundeigenschaften der Moleküle deuten zu können.

La théorie de la structure électronique des hydrures diatomiques est étudiée, où la charge nucléaire du second noyau est variable. A l'aide d'un facteur d'échelle dépendant de la charge nucléaire et de la distance internucléaire l'équation de Schrödinger peut être mise dans une forme convenable à un calcul perturbateur. Les énergies de nullième et de premier ordre sont calculées pour quelques séquences isoélectroniques; mais la comparaison de l'expérience montre qu'il faut des termes de plus grand ordre pour expliquer les propriétés fondamentales des molécules.

1. Introduction

One of the most fruitful ideas in the study of atomic structure has been that of an isoelectronic sequence. Its importance in the analysis of spectra has been considerable since the gross features of spectra depend very simply on the nuclear charge Z, so that interpolations and extrapolations are easy and profitable. The importance of isoelectronic sequences in the theory of atoms was first appreciated by Hylleraas [7] who showed that the Schrödinger equation could be reformulated so that its solution could be expressed as a power series in Z^{-1}. Another novelty of this treatment is that the solution is obtained using perturbation theory instead of the more usual variation theory. In practice, the perturbation equations are solved by a variational method and can be computed to high accuracy and to high orders [8]. A further advantage of this theory is that, by repeating the calculation using a determinantal wavefunction, the variation of the correlation energy as a function of Z can be discussed [1, 9.]

The principal purpose of the present paper is to show how this idea of an isoelectronic sequence can be extended to diatomic hydrides. By another reformulation the theory is put into a very similar form to the atomic theory and many of the theoretical advantages of this theory are retained. The practical utility of the theory is very limited, however, by the fact that in each sequence there are only a few molecules which are stable with respect to dissociation.

2. Perturbation expansion for non-degenerate wavefunctions

There are several different types of isoelectronic sequence of molecules and each will have its own form of theory. In this paper the sequences are of diatomic hydrides partly because the nuclear charge of the other nucleus dominates the potential and makes these most like the atomic sequences and partly because the zero order perturbation equations can be solved exactly.

The electronic structure of a diatomic hydride is governed by the Hamiltonian

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i Z/r_i - \sum_i 1/r_{iH} + \sum_{i<j} 1/r_{ij} \tag{1}$$

where Z is the nuclear charge and r_i and r_{iH} the distances between the ith electron and the nucleus and the proton respectively. For reasons which will emerge later this Hamiltonian will be written as

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i (Z-\alpha)/r_i - \alpha\sum_i 1/r_i - \sum_i 1/r_{iH} + \sum_{i<j} 1/r_{ij} \tag{2}$$

where α is a parameter which will be determined later. The units implied in this Hamiltonian are the usual atomic units. To obtain a more useful form of the Hamiltonian the unit of charge is changed to $e\sqrt{Z-\alpha}$ without changing the units of mass or of action. The unit of length is then $(Z-\alpha)$ Bohrs and of energy $(Z-\alpha)^2$ Hartrees. In these units the Hamiltonian becomes

$$H = H_0 + (Z-\alpha)^{-1} H_1 \tag{3}$$

with

$$H_0 = \sum_i \left(-\frac{1}{2}\nabla_i^2 - 1/r_i\right) \tag{4}$$

$$H_1 = \sum_{i>j} 1/r_{ij} - \alpha\sum_i 1/r_i - \sum_i 1/r_{iH}. \tag{5}$$

The importance of this step in the argument is that it enables the zero-order wavefunction to be found exactly since the zero-order Hamiltonian H_0 separates into hydrogen atom Hamiltonians for each electron and the zero-order wavefunction Ψ_0 will consist of one or more determinants of hydrogen atom orbitals. In this section it will be assumed that the ground state energy is non-degenerate so that Ψ_0 is a single determinant. The perturbation expansion now has the form

$$\Psi = \Psi_0 + (Z-\alpha)^{-1}\Psi_1 + \cdots \tag{6}$$

$$W = W_0 + (Z-\alpha)^{-1} W_1 + (Z-\alpha)^{-2} W_2 + (Z-\alpha)^{-3} W_3 + \cdots. \tag{7}$$

This use of $(Z-\alpha)^{-1}$ as the expansion parameter instead of Z^{-1} greatly assists the convergence of the series for an atom [*4*] and is even more important for a molecule. Each term in the expansion of the wavefunction determines two terms in the expansion of the energy [*3*] so that, for example, if Ψ_0 is normalized the first two terms in the energy are

$$W_0 + (Z-\alpha)^{-1} W_1 = \int \Psi_0^* [H_0 + (Z-\alpha)^{-1} H_1]\, \Psi_0\, d\tau \tag{8}$$

or, in the original Hartree units

$$(Z-\alpha)^2 \int \Psi_0^* H \Psi_0 \, d\tau. \tag{9}$$

This is the energy that would have been obtained using a trial wavefunction in the form of a determinant of hydrogen atom functions each with the scale factor $(Z-\alpha)$. This suggests that the value of α should be fixed by minimizing those first two terms for each value of the internuclear distance. The value of α found in this way may not be the best one to ensure the most rapid convergence of the series for the energy but it should be sufficiently good for present purposes.

When the internuclear distance vanishes the electronic Hamiltonian reduces to that for the united atom. At the other limit when the internuclear distance is very large the proton is effectively removed leaving all the electrons around the other nucleus. The resulting ion, which will be called the separated ion, is isoelectronic with the united atom but has a nuclear charge less by one. Thus if α increases by one as the internuclear distance varies from zero to infinity the coefficients in the energy expansion must be the same at both limits. In particular, the method of choosing α adopted above satisfies this requirement and so will help to keep the variations in the coefficients with internuclear distance small. This emphasis on a smooth curve connecting the two limits leads unfortunately to several complications. Thus, for neutral molecules, the separation into ions at large distances means that the calculated energy does not follow one energy eigenvalue but crosses smoothly over several in order to preserve the ionic nature of the wavefunction. If the crossings are far from the equilibrium distance and if allowances are made when calculating dissociation energies this passing from one potential to another may not be a major disadvantage. Another complication is that there are states which are important for certain nuclear charges and for intermediate distances which cannot easily be brought into the theory since they correspond to continuum states at the limits.

The form of the electronic energy in terms of the original Hartree units is now

$$W = (Z-\alpha)^2 W_0 + (Z-\alpha) W_1 + W_2 + (Z-\alpha)^{-1} W_3 + \cdots \tag{10}$$

where α, W_0 and W_1, can be calculated using only the hydrogen atom orbitals. The various W_r are functions of the modified internuclear distance which is

$$\varrho = (Z-\alpha) R, \tag{11}$$

where R is the actual internuclear distance in Bohrs.

3. Application to the one and two electron sequences

The relations between this perturbation theory and other theories can be conveniently illustrated using the one electron sequence. Since the electron is in the field of a nucleus of charge Z and a proton separated at distance R from it, the electronic Hamiltonian, in atomic units, is

$$H = -\frac{1}{2}\nabla^2 - (Z-\alpha)/r - (\alpha/r + 1/r_H). \tag{12}$$

When the unit of charge is increased to $e\sqrt{Z-\alpha}$, the Hamiltonian becomes

$$(-\frac{1}{2}\nabla^2 - 1/r) - (Z-\alpha)^{-1}(\alpha/r + 1/r_H) \tag{13}$$

where the separation of the nuclei is now ϱ.

The exact zero order wavefunction is

$$\Psi_0 = \pi^{-\frac{1}{2}} e^{-r} \tag{14}$$

and the energy expansion has

$$W_0 = -\frac{1}{2} \tag{15}$$

and

$$\begin{aligned} W_1 &= -\int \Psi_0 \, (\alpha/r + 1/r_H) \, \Psi_0 \, d\tau \\ &= -\alpha - \varrho^{-1} \, [1 - (1 + \varrho)e^{-2\varrho}]. \end{aligned} \tag{16}$$

By minimizing the first two terms in the energy with respect to α, α is determined as

$$\alpha = -(1 + 2\varrho)e^{-2\varrho} \tag{17}$$

and varies from -1 at $\varrho = 0$ to 0 as $\varrho \to \infty$. At both limits the perturbation vanishes and Ψ_0 becomes the entire exact solution.

From these first two terms in the energy an approximation to the energy potential can be obtained but it is not satisfactory. The equilibrium distance R_0, for example, is obtained from the equation

$$\frac{d}{dR} (W + Z/R)_{R=R_0} = 0. \tag{18}$$

This reduces for H_2^+ to the equation

$$(1 + 2\,\varrho_0 + 2\,\varrho_0^2)\; e^{-2\varrho_0} = 0 \tag{19}$$

which cannot be satisfied for any finite value of ϱ_0 which means that the potential is purely repulsive.

The third term in the energy series can be included in the treatment in various ways. The perturbation calculation of DALGARNO and LYNN [2] gives this term exactly but only for $\alpha = 0$. An alternative procedure would be to use the known energy curve for H_2^+ to fit a suitable form for the third term. The details of this process are discussed later. In principle this could be used to predict the energy curves for other values of Z but in practice there are two complications. The first is that the hydrogen molecular ion is the only member of the sequence to have a stable equilibrium internuclear distance. The second is that for $Z = 1$ the two nuclei become identical and a wavefunction of the form assumed is no longer sufficiently accurate to give good results. The identity of the centres leads, in fact, to an unusually large perturbation and so is not properly used in an extrapolation to other Z.

Unfortunately, some of the difficulties of the one-electron sequence are still found in the two-electron sequence although others are eliminated. The Hamiltonian is again modified by a change of scale and rearranged into the form

$$\begin{aligned} &(-\tfrac{1}{2}\nabla_1^2 - 1/r_1) + (-\tfrac{1}{2}\nabla_2^2 - 1/r_2) + \\ &+ (Z - \alpha)^{-1} \, (1/r_{12} - 1/r_{1H} - 1/r_{2H} - \alpha/r_1 - \alpha/r_2). \end{aligned} \tag{20}$$

The exact zero order wavefunction is

$$\Psi_0 = \pi^{-1} \exp{(-r_1 - r_2)} \tag{21}$$

and the first two energy terms are

$$W_0 = -1 \tag{22}$$

$$\begin{aligned} W_1 &= \int \Psi_0 \,(1/r_{12} - 1/r_{1H} - 1/r_{2H} - \alpha/r_1 - \alpha/r_2)\Psi_0 \, d\tau \\ &= -2/\varrho\,[1-(1+\varrho)e^{-2\varrho}] + 5/8 - 2\alpha. \end{aligned} \tag{23}$$

If the best value of α is defined as the one which minimizes these two terms in the energy then

$$\alpha = 5/16 - (1+2\varrho)e^{-2\varrho} \tag{24}$$

so that α varies from $-11/16$ at $\varrho = 0$ to $5/16$ as $\varrho \to \infty$.

The equilibrium internuclear distance is found by differentiating the total energy and, for $Z = 1$ and the best value of α, this leads to

$$1 = (2 + 4\varrho_0 + 4\varrho_0^2)e^{-2\varrho_0} \tag{25}$$

which may be solved to give

$$\varrho_0 = 1.336. \tag{26}$$

This results in a calculated separation of

$$R_0 = 1.42 \text{ Bohrs}. \tag{27}$$

compared with the experimental value of 1.40 B. Similarly the force constant is calculated to be 0.301 compared with the experimental 0.371. For $Z = 2$, however, the potential given by the first two terms is purely repulsive.

4. Perturbation expansion for degenerate wavefunctions

For most states of most diatomic hydrides the perturbation method described above needs to be modified before it can be applied. This is due to the degeneracy of the zero-order wavefunction which arises because of the degeneracy of the hydrogen atom orbitals. Thus, in general, there will be a number of determinantal wavefunctions with the same energy and the appropriate linear combination has to be found using degenerate perturbation theory and diagonalizing the matrix of the perturbation. An alternative formulation which leads to the same result is that the energy should be minimized with respect to the coefficients in the linear combination. This shows that the perturbation now effects the wavefunction to zero order and so leads to an additional lowering of the first order correction to the energy. When the best linear combination of determinants has been substituted for Ψ_0 the discussion and equations in § 2 remain valid.

As the number of electrons in the molecule is increased so the number of degenerate wavefunctions tends to increase though there are several counteracting features. The first of these is the Pauli principle and this is sometimes sufficient, for example in the ground state of the 10 electron sequence, to lead to non-degeneracy. The second is the existence of selection rules due to spin and to the axial symmetry ($C_{\infty h}$) which still apply. The $^3\Sigma^-$ ground state of the 8 electron sequence, for example, has no degeneracy except that due to the triplet which can be resolved easily by using S_z.

The calculation of the matrix elements of the energy with respect to those zero-order atomic wavefunctions is made easier by certain selection rules which apply to the different terms in the energy. Since part of the perturbation is a one-electron operator its matrix elements vanish between wavefunctions which differ in respect to two or more orbitals. On the other hand, the two-electron part has spherical symmetry and so has zero matrix elements between wavefunctions of different spherical symmetry even though they have the same axial symmetry.

This extension of the theory to include degeneracy means that effects such as the angular correlation effects discussed by LINDERBERG and SHULL [9] are now included in the theory.

5. The total energy, equilibrium distance and force constant

The expansion of the total electronic energy for the N electron sequence, whether degeneracy occurs or not, has the form

$$W = (Z - \alpha)^2 W_0 + (Z - \alpha) W_1 + W_2 + \cdots. \tag{28}$$

The first coefficient W_0 is the sum of contributions of $-{}^1/_2$ for each $1s$ electron and of $-{}^1/_8$ for each $2s$ or $2p$ electron and is independent of ϱ. For the non-degenerate case, W_1 is the mean value of the perturbation and so depends on both ϱ and α. When there is degeneracy, W_1 is determined by diagonalizing a finite matrix whose elements are the matrix elements of H_1. Now α appears in H_1 as a multiple of a one-electron spherical potential and the selection rules ensure that α will then enter only the diagonal matrix elements and with the same coefficient. Thus, in either event W_1 has the form

$$W_1 = f(\varrho) - C\alpha, \tag{29}$$

where f depends only on ϱ and C is a constant which has the value $-2\,W_0$.

The total energy, E, of a diatomic hydride when the electronic energy is taken up to the third term is now

$$E = (Z - \alpha)^2 W_0 + (Z - \alpha)(f - C\alpha) + W_2(\varrho) + Z/R. \tag{30}$$

Although W_2 will not be calculated here it is desirable to include it in order to be able to estimate its effect empirically. The scale factor α is determined by minimization so that, at constant R,

$$\frac{dE}{d\alpha} = C\alpha - f - \varrho f' - R\,W_2' = 0. \tag{31}$$

When W_2 is omitted this equation determines α as a function of ϱ and hence of R. The equilibrium internuclear distance, R_0, is defined as the value which minimizes the energy so that it satisfies

$$\left(\frac{dE}{dR}\right)_{R_0} = \left(\frac{\partial E}{\partial R} + \frac{dE}{d\alpha}\frac{d\alpha}{dR}\right)_{R_0} = 0 \tag{32}$$

and, since α satisfies

$$\frac{dE}{d\alpha} = 0 \tag{33}$$

this condition simplifies to

$$\frac{\partial E}{\partial R} = [(Z-\alpha)^2\,(f' - Z/\varrho^2) + (Z-\alpha)\,W_2']_{R_0} = 0. \tag{34}$$

When W_2' is omitted this equation for R_0 can be written as

$$f'\,(\varrho_0) = Z/\varrho_0^2 \tag{35}$$

where

$$Z - \alpha\,(\varrho) = \eta,\ Z - \alpha\,(R_0) = \eta_0,\ \varrho_0 = R_0\,\eta_0. \tag{36}$$

This equation is very similar in form to one obtained earlier [*5*], using a scaled form of the Platt model [*10*], viz

$$\frac{\partial V}{\partial \varrho_0} = Z/\varrho_0^2 \tag{37}$$

where V is the electronic potential energy and this reduces to the more explicit form

$$4\,\pi \int_0^{\varrho_0} \gamma\,(r)\,r^2\,dr = Z \tag{38}$$

where $\gamma\,(r)$ is the spherically symmetric electron density due to the zero-order wavefunction.

The force constant, k, is defined as the second derivative of the total energy at R_0 and, after some manipulation, can be reduced to the formula

$$k = \left(\frac{d^2E}{dR^2}\right)_{R_0} = \eta_0^4 \left\{ f''(\varrho_0) + 2\,Z/\varrho_0^3 + W_2''(\varrho_0)/\eta_0 - [W_2'(\varrho_0)]^2/C\eta_0^3 \right\} / \\ \left\{ \eta_0 + \varrho_0^2\,[f''(\varrho_0) + 2\,Z/\varrho_0^3 + W_2''(\varrho_0)/\eta_0]/C \right\}. \tag{39}$$

When W_2 is omitted this takes the form

$$k = \eta_0^4 \left\{ f''(\varrho_0) + 2\,Z/\varrho_0^3 \right\} / \left\{ \eta_0 + \varrho_0^2\,[f''(\varrho_0) + 2\,Z/\varrho_0^3]/C \right\} \tag{40}$$

which is again similar to the corresponding formula obtained earlier [*5*].

6. Application to the four-electron sequence

The application of the theory when there is degeneracy can be illustrated by reference to the four-electron sequence. The ground state of this sequence has the symmetry $^1\Sigma$ and there are four degenerate zero-order wavefunctions which contribute to it. These are, is spectroscopic notation,

$(1s)^2\ (2s)^2\ {}^1S$
$(1s)^2\ (2s,\,2p_z)\ {}^1P$ ($L_z = 0$ component)
$(1s)^2\ (2p)^2\ {}^1S$
$(1s)^2\ (2p)^2\ {}^1D$ ($L_z = 0$ component).

These give rise to a 4 × 4 matrix whose eigenvalues determine W_1. The elements in this matrix are simplified by using the selection rules mentioned above. The integrals involving the electrostatic repulsions are available in LINDERBERG and SHULL [*9*]. The parameter α appears explicitly only on the diagonal and can be omitted from the diagonalization. The remaining matrix elements are either constants or are functions of ϱ. The matrix has to be diagonalized and its eigenvalues found for a range of values of ϱ in order to determine $f\,(\varrho)$.

The evaluation of the matrix elements for each ϱ and the calculation of the eigenvalues have been programmed for the English Electric DEUCE computer. Care is needed in evaluating the matrix elements since, for certain ϱ, they involve considerable cancellations between polynomials and exponentials. This is overcome by arranging the formula so that these exponentials are evaluated as power series and the cancellation carried out analytically. The eigenvalues were calculated for values of ϱ at intervals of 0.25 Bohr between $\varrho = 0.25$ Bohr and $\varrho = 15$ Bohr. The derivatives of f were found by numerical differentiation. The equilibrium value of ϱ was found from the equation by inverse interpolation and then the corresponding value of α. The internuclear distance R_0 and the force constant k are readily deduced. The results obtained for the ground state and for the first excited state which has the same symmetry as the ground state are shown in the table. The experimental results quoted in comparison are taken from HERZBERG [*6*].

Table. *Calculated and experimental internuclear distances and force constants*

Molecule	State	$Z - \alpha_0$	ϱ_0 (Bohrs)	R_0 (Å)	R_{exp} (Å)	k (10^5 dynes/cm)	k_{exp} (10^5 dynes/cm)
LiH	ground	2.443	5.015	1.086	1.595	4.263	1.026
	excited	2.416	4.596	1.007	2.596	5.791	0.029
BeH$^+$	ground	3.378	8.444	1.323	1.312	0.812	2.633
	excited	3.342	6.442	1.020	1.609	5.541	1.162

The large discrepancies between calculation and experiment suggest very strongly that $W_2(\varrho)$ needs to be included in the calculation before significant predictions can be made. This is the next term in the perturbation series and could be calculated by finding the first order correction to the wavefunction. Instead of doing this its effect will be estimated empirically.

Since $W_2(\varrho)$ does not depend explicitly on Z its effect can be estimated by equating theory and experiment for one molecule and using the results to predict the effect for another molecule. Since W_2 ought to be a smooth function of ϱ in the neighbourhood of the equilibrium it is expanded as a Taylor series about the equilibrium ϱ_0 for the first molecule

$$W_2(\varrho) = W_2(\varrho_0) + (\varrho - \varrho_0) W_2'(\varrho_0) + \frac{1}{2}(\varrho - \varrho_0)^2 W_2''(\varrho_0). \tag{41}$$

The experimental internuclear distance and force constant for the first molecule are then used to determine $W_2'(\varrho_0)$ and $W_2''(\varrho_0)$. The value of $W_2(\varrho_0)$ could be fixed if the experimental total energy were known accurately enough but it is usually better to leave it undetermined.

For the four-electron sequence the molecule *LiH* was taken as the known molecule and its data used to predict corresponding results for *BeH*$^+$. By eliminating W_2 from the equations defining ϱ_0 and α_0 it follows that

$$C\,\alpha_0 = f(\varrho_0) + Z/\varrho_0 \tag{42}$$

so that the relation between α_0 and ϱ_0 is unchanged by the inclusion of W_2. The value of ϱ corresponding to equilibrium is changed, however, because of the extra term. Its new value ϱ_0', may be determined by using the experimental distance, R_{exp}, the relation between α_0 and ϱ_0 and the iteration formula

$$(\varrho_0')_{n+1} = \{Z - \alpha\,[(\varrho_0')_n]\}\,R_{exp}. \tag{43}$$

Once the consistent value of ϱ_0' has been found the original definition of the equilibrium distance becomes an equation for $W_2'\,(\varrho_0')$. The corresponding value of $W_2''\,(\varrho_0')$ follows from the experimental force constant. For the ground state of *LiH* the consistent value of ϱ_0' is 7.332 and the expansion of W_2 becomes

$$W_2\,(\varrho) = W_2\,(\varrho_0') - (\varrho - \varrho_0')\,0.038\,025 + \frac{1}{2}\,(\varrho - \varrho_0')^2\,0.015\,289. \tag{44}$$

With this form for W_2 the results for BeH^+ were re-calculated and are 1.512 Å for R_0 and 2.301×10^5 dynes/cm for k. The former is made worse by the inclusion of W_2 although the latter is considerably improved. A secondary result which follows from this calculation is that E' has no zero for $Z > 4.1$ in the ground state and for $Z > 4.5$ in the excited state. Thus the theory predicts that the energy curves for CH^{++} and higher members of the sequence are purely repulsive.

While these numerical results are disappointing they are better than might have been expected physically. The *LiH* molecule is wellknown to be close to ionic in its binding with the hydrogen negative, yet this theory uses a wavefunction in which the electrons are all centered on the *Li*. The mixture of determinants ensures, however, that the zero-order wavefunction does have a substantial dipole moment in the direction of the proton.

7. Conclusions

The first quantitative results of this theory of diatomic hydrides are very much less encouraging than for the corresponding theory of atomic isoelectronic sequences. This must be attributed to the fact that the zero-order wavefunction is a much cruder approximation in relation to the molecules than to the atoms. The theory will have to be carried to higher order before significant agreement with experiment can be expected.

The significance of this theory is that it is a method of investigating molecular structure using perturbation theory and stressing the possibility of varying the nuclear charge. By using, as a first approximation, a wavefunction which interpolates between the united atom and the separated ion it also provides some interesting cross-connections between various physical ideas. Its relation to the Platt model is particularly close although its restriction to hydrogenic orbitals instead of self-consistent ones makes the numerical results much less accurate. A modification of the theory to permit more accurate orbitals without complicating the expansion is very desirable.

Although the applications in this paper have been restricted to diatomic hydrides because these are best known it is trivial to extend the theory to polyatomic molecules which have one heavy atom and a number of hydrogens.

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