The Calculation of Zero-Point Energies of Molecules by Perturbation Methods*†

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Two methods are proposed for calculating zero-point energies of molecules. The first makes use of the fact that one can easily write down the quantum mechanical Hamiltonian for a vibrating system. The zero-point energy can then be obtained by a perturbation scheme without solving the secular equation. The second method requires a knowledge of the normal modes and frequencies of a reference molecule, but then enables one to calculate isotope effects by a perturbation scheme. The methods are applied to some examples and the convergence of the perturbation series is investigated. The approximate validity of the law of the mean for the isotope effect on zero-point energies is explored within the framework of the methods.

The present paper concerns itself with the calculation of the vibrational zero-point energy of a molecule. Vibrational-rotational interaction will not be considered, and the potential energy surface for the vibrational motion of the atomic nuclei will be considered to be harmonic. The zero-point energy of a molecule is of fundamental interest since it represents the minimum energy of the vibrating system with respect to the minimum (for a stable molecule – for a transition state in a chemical reaction more care must be taken in the definition) in the potential energy surface. Since isotopically substituted molecules possess the same vibrational potential energy surfaces within the framework of the Born–Oppenheimer approximation, the zero-point energy differences between isotopically substituted molecules are very important in the theoretical consideration of isotope effects on equilibria and also on reaction rates.

I. The Usual Approach

It is not the intention to review here the theory of molecular vibrations; the reader is referred to the literature [1] for such a discussion. For the present purposes, the potential (V) and kinetic (T) energies of the N atomic molecule are expressed in terms of $3N-6$ independent internal displacement coordinates q_i and their conjugate momenta p_i (for a linear molecule $3N-5$ coordinates). Thus

$$2V = \sum f_{ij} q_i q_j , \tag{1}$$

$$2T = \sum g_{ij} p_i p_j . \tag{2}$$

Here the f_{ij} are force constants and are the elements of the so-called F matrix; while the g_{ij}, the elements of the G matrix, can be easily evaluated in terms of the atomic masses and geometry of the molecule as has been shown by Wilson [1]. The matrix F is independent of isotopic substitution while G does depend on isotopic substitution. The $3N-6$ normal frequencies ν_i of the system are obtained by solving the secular equation involving the F and G matrices in one of its many alternative forms [1]. One can also determine the transformation between normal coordinates Q_i and internal coordinates

$$Q_j = \sum_{r}^{3N-6} A_{jr} q_r . \tag{3}$$

In terms of the normal coordinates the potential and kinetic energies are re-expressed as

$$2V = \sum^{3N-6} 4\pi^2 \nu_i^2 Q_i^2, \quad 2T = \sum P_i^2 \tag{4}$$

where P_i is the momentum conjugate to Q_i. The Hamiltonian for the quantum mechanical problem

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[1] See, for instance, E. B. Wilson, jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill Book Company, Inc., New York 1955.

is then

$$H = T + V = \frac{1}{2}\left(\sum P_i^2 + \sum 4\pi^2 \nu_i^2 Q_i^2\right) = \frac{1}{2}\sum^{3N-6}(P_i^2 + 4\pi^2 \nu_i^2 Q_i^2). \quad (5)$$

Now $P_i^2 + 4\pi^2 \nu_i^2 Q_i^2$ is the HAMILTONian of a harmonic oscillator which has quantum mechanical energy levels $E_n = (n + 1/2)\, h\nu_i$ $(n = 1, 2, 3, \ldots)$. The quantum mechanical description of the system according to eq. (5) corresponds then to $3N-6$ independent harmonic oscillators corresponding to the $3N-6$ normal frequencies ν_i of the classical system (this description of the system is, in fact, the same as the classical one). The quantum mechanical ground state energy of the system corresponds to each oscillator in its respective ground state

$$E_0 = \frac{1}{2}\sum^{3N-6} h\nu_i. \quad (6)$$

II. The Perturbation Method

Above, the standard method for determining the zero-point energy of the vibrations of a molecule was outlined. This method involves the solution of the secular equation. In this section a method for obtaining the zero-point energy without solving the secular equation (at least not for every isotopic species) will be proposed [2, 3]. The type of approach used rests on the fact that the HAMILTONian obtained from equations (1) and (2) is in proper form (i. e. in terms of coordinates and their conjugate momenta) for quantum mechanical use,

$$H = T + V = (1/2)\sum_{i,j}^{3N-6}(g_{ij}\, p_i\, p_j + f_{ij}\, q_i\, q_j). \quad (7)$$

It must now be remembered that the ground state energy of this HAMILTONian is just the zero-point energy.

In the methodology which shall be designated as A, the quantum mechanical ground state energy corresponding to the HAMILTONian (7) is determined by breaking up this HAMILTONian into two parts – H_0, which will be designated as the unperturbed HAMILTONian and H_1, which will be designated as the perturbation. Thus

$$H = H_0 + H_1, \quad (8)$$

$$H_0 = (1/2)\sum_{i}^{3N-6}(g_{ii}\, p_i^2 + f_{ii}\, q_i^2), \quad (9)$$

$$H_1 = (1/2)\sum_{i \neq j}(q_{ij}\, p_i\, p_j + f_{ij}\, q_i\, q_j) = \sum_{i<j}(g_{ij}\, p_i\, p_j + f_{ij}\, q_i\, q_j). \quad (10)$$

The HAMILTON H_0 describes $3N-6$ independent oscillators corresponding to $3N-6$ internal coordinates which carry out independent motion. The zero-point energy corresponding to the unperturbed HAMILTONian is obviously

$$E_0^0 = \frac{1}{2}\sum^{3N-6}\frac{h}{2\pi}(f_{ii}\, g_{ii})^{1/2} = \frac{1}{2}\sum^{3N-6} h\nu_i \quad (11)$$

where the superscript zero refers to the "zeroeth" order approximation in the perturbation theory. The wave functions of the unperturbed HAMILTONian are just product wave functions of $3N-6$ independent oscillators. From now on ν_i will be used to refer to the frequencies of the unperturbed problem.

The contribution of the perturbation H_1 to the zero-point energy is evaluated by means of quantum mechanical perturbation theory [4]. The first order perturbation correction to the ground state energy is the average of the perturbation over the ground state. The unperturbed ground state wave function is

$$\Psi_0 = \psi_0(q_1)\ \psi_0(q_2) \ldots \psi_0(q_{3N-6}), \quad (12)$$

where the ψ_0's refer to ground state harmonic oscillator wave functions. The contribution of a term $g_{ij}\, p_i\, p_j + f_{ij}\, q_i\, q_j$ to the first order perturbation correction is given by

$$\begin{aligned}\Delta E_0^1 &= \int\ldots\int \Psi_0^*(g_{ij}\, p_i\, p_j + f_{ij}\, q_i\, q_j)\ \Psi_0\, \mathrm{d}q_1 \cdots \mathrm{d}q_{3N-6} \\ &= \Big[g_{ij}\int \psi_0^*(q_i)\, p_i\, \psi_0(q_i)\, \mathrm{d}q_i \int \psi_0^*(q_j)\, p_j\, \psi_0(q_j)\, \mathrm{d}q_j \\ &\quad + f_{ij}\int \psi_0^*(q_i)\, q_i\, \psi_0(q_i)\, \mathrm{d}q_i \int \psi_0^*(q_j)\, q_j\, \psi_0(q_j)\, \mathrm{d}q_j\Big] \\ &\quad \cdot \prod_{s \neq i,j}\int \psi_0^*(q_s)\ \psi_0(q_s)\, \mathrm{d}q_s. \end{aligned} \quad (13)$$

Use has been made here of the fact that the unperturbed oscillators are all independent. The pro-

[2] Another method for circumventing the solution of the secular equation has been discussed in the preceding two papers, J. BIGELEISEN and P. GOLDSTEIN, Z. Naturforschg. **18 a**, 205 [1963], and J. BIGELEISEN, R. E. WESTON, JR., and M. WOLFSBERG, Z. Naturforschg. **18 a**, 210 [1963].

[3] Perturbation methods may also be employed to find the ν_i's by the secular equation method. This approach has not been investigated here.

[4] P. M. MORSE and H. FESHBACH, Methods of Theoretical Physics, McGraw-Hill Book Company, Inc., New York 1953, p. 1004.

duct of integrals multiplying the term in brackets is, of course, just equal to unity since the wave functions ψ_0 are normalized. Integrals of the types in the brackets can be very easily evaluated and their values have also been tabulated in many publications [5]. All the integrals in brackets are equal to zero. Thus the perturbation H_1 makes no contribution to the zero-point energy to first order.

The second order perturbation contribution from H_1 is given by

$$\Delta E_0^2 = \sum_{n \neq 0} \frac{|\int \cdots \int \Psi_0^* H_1 \Psi_n \, dq_1 \ldots dq_{3N-6}|^2}{E_0^0 - E_n^0} \quad (14)$$

where Ψ_n refers to any excited state of the unperturbed HAMILTONian with corresponding energy E_n^0. Thus Ψ_n may refer to the state in which the i^{th} oscillator is in its first excited state while all the other oscillators are in their respective ground states; in this case $E_0^0 - E_n^0 = -h\nu_i$. It is obvious that the second order perturbation contribution must be negative. Following the same reasoning as that employed in studying the first order perturbation term, one finds, for a term $g_{ij} p_i p_j + f_{ij} q_i q_j$, that only that state Ψ_n contributes to ΔE_0^2 in which both the i^{th} and j^{th} oscillator are in their first excited states and the other oscillators are in their ground states. Moreover the contribution of this term is

$$-\frac{h}{4}\left[-\frac{g_{ij}}{(g_{ii}\, g_{jj})^{1/2}} + \frac{f_{ij}}{(f_{ii}\, f_{jj})^{1/2}}\right]^2 \frac{\nu_i \nu_j}{\nu_i + \nu_j} . \quad (15)$$

ν_i and ν_j are defined by (11). Thus, the total zero-point energy up to second order perturbation theory is given by

$$E_0^2 = \frac{1}{2}\sum_{i}^{3N-6} h\nu_i - \frac{1}{4}\sum_{i<j}\left[-\frac{g_{ij}}{(g_{ii}\, g_{jj})^{1/2}} + \frac{f_{ij}}{(f_{ii}\, f_{jj})^{1/2}}\right]^2 \frac{h\nu_i \nu_j}{\nu_i + \nu_j} . \quad (16)$$

It will be seen in the examples that E_0^2 converges fairly well to the true zero-point energy. Proceeding to higher orders of perturbation theory presents no difficulty in principle but the bookkeeping involved in cataloguing all the terms tends to be tedious. No general formulae will be given for higher order perturbation theory and little use will be made for the present of such higher orders of perturbation.

Methodology A discussed above is used to calculate the zero-point energy of a system. The isotope effect on the zero-point energy may be obtained by calculating the zero-point energies for isotopic molecules by means of methodology A. Methodology B which will be described briefly now is used only to calculate isotope effects. In this methodology the HAMILTONian of one isotopic system – the reference system (say the isotopically unsubstituted system) is taken as the unperturbed HAMILTONian. The isotope effect on the kinetic energy expression is the perturbation. The total perturbation energy is then the isotope effect on the zero-point energy. Let g' refer to the isotopically substituted system. Then

$$H = \frac{1}{2}\sum_{i,j} g'_{ij} p_i p_j + f_{ij} q_i q_j = H_0 + H_1 \quad (17)$$

$$\text{where } H_0 = \frac{1}{2}\sum_{i,j}(g_{ij} p_i p_j + f_{ij} q_i q_j) = \frac{1}{2}\sum_i (P_i^2 + 4\pi^2 \nu_i^2 Q_i^2) \quad (18)$$

$$\text{and } H_1 = \frac{1}{2}\sum_{i,j}(g'_{ij} - g_{ij})\, p_i p_j = \frac{1}{2}\sum_{\substack{i,j \\ r,s}} (g'_{ij} - g_{ij})\, A_{ir} A_{js} P_r P_s . \quad (19)$$

P and Q refer to the normal modes of the reference molecule. As described in eqs. (17), (18) and (19) this perturbation approach requires a knowledge of the frequencies ν_i of the reference molecule and also the corresponding matrix A defined by eq. (3). The unperturbed eigenfunctions are now products of the eigenfunctions of the $3N-6$ independent normal modes of the reference system. The calculation of the change in zero-point energy from the perturbation term H_1 proceeds similarly as in methodology A. H_1 contains only quadratic terms in P. Since H_1 will contain terms in P_i^2 the first order perturbation correction will no longer vanish. It is somewhat surprising that this type of perturbation expansion converges rather well even for the case of hydrogen isotopic substitution.

III. Numerical Examples

a) The hydrogen molecule

A very simple numerical example of methodology B is furnished by consideration of the hydrogen molecule. For the first calculation, H_2 is taken as the reference molecule and it is attempted to calculate the zero-point energies of HD and of D_2. The force constant corresponding to the stretching co-

[5] See, for instance, E. B. WILSON, JR., J. C. DECIUS, and P. C. CROSS, Molecular Vibrations, McGraw-Hill Book Company, Inc., New York 1955, Appendix III.

ordinate r with corresponding conjugate momentum p_r is taken to be k so that

$$2V = k r^2. \tag{20}$$

The kinetic energy expressions for the three molecules are found remembering [1] that $g_{rr} = \frac{1}{m_1} + \frac{1}{m_2}$,

$$2T_{H_2} = \frac{2}{m_H} p_r^2, \quad 2T_{HD} = \left(\frac{1}{m_H} + \frac{1}{m_D}\right) p_r^2, \quad 2T_{D_2} = \frac{2}{m_D} p_r^2 \tag{21}$$

where m refers to the relevant atomic mass. The zero-point energy for the reference molecule, H_2, is given by

$$E_0 = \frac{1}{2} h \frac{1}{2\pi} \left(\frac{2k}{m_H}\right)^{1/2} = \frac{1}{2} h \nu_{H_2}. \tag{22}$$

The normal coordinate for H_2 and corresponding momentum are respectively

$$Q = (m_H/2)^{1/2} r, \quad P = (2/m_H)^{1/2} p_r. \tag{23}$$

In terms of this transformation

$$2H_{H_2} = P^2 + 4\pi^2 \nu_{H_2}^2 Q^2.$$

One obtains then for the perturbation H_1 for the cases of HD and D_2 respectively

$$(H_1)_{HD} = H_{HD} - H_{H_2} = \frac{1}{2}\left(\frac{1}{m_D} - \frac{1}{m_H}\right) p_r^2 = \frac{1}{4}\left(\frac{m_H}{m_D} - 1\right) P^2 \tag{24}$$

and

$$(H_1)_{D_2} = H_{D_2} - H_{H_2} = \left(\frac{1}{m_D} - \frac{1}{m_H}\right) p_r^2 = \frac{1}{2}\left(\frac{m_H}{m_D} - 1\right) P^2. \tag{25}$$

It is immediately seen that the perturbation expression for D_2 is twice that for H_2. This means that the first order perturbation correction to the zero-point energy of the reference molecule (H_2) is twice as big for D_2 as for HD. Thus, to this order of approximation, the so-called law of the mean, which will be discussed later, is valid. Since $[(m_H/m_D) - 1]$ is negative, the higher order perturbation terms will tend to make the total perturbation energy (i. e. $\Delta E_0^1 + \Delta E_0^2 + \ldots$) for D_2 more than twice as large as for HD. One finds for the first order perturbation term

$$(\Delta E_0^1)_{HD} = \frac{1}{4}\left(\frac{m_H}{m_D} - 1\right) \int \psi_0 P^2 \psi_0 \, dQ = \frac{1}{8}\left(\frac{m_H}{m_D} - 1\right) h \nu_{H_2} \tag{26}$$

and similarly

$$(\Delta E_0^1)_{D_2} \frac{1}{4}\left(\frac{m_H}{m_D} - 1\right) h \nu_{H_2}. \tag{27}$$

In second order perturbation

$$(\Delta E_0^2)_{HD} = \frac{1}{16}\left(\frac{m_H}{m_D} - 1\right)^2 \left(\frac{1}{-2h\nu}\right) \left| \int \psi_0 P^2 \psi_2 \, dQ \right|^2 = -\frac{1}{64}\left(\frac{m_H}{m_D} - 1\right)^2 h \nu_{H_2} \tag{28}$$

and

$$(\Delta E_0^2)_{D_2} = -\frac{1}{16}\left(\frac{m_H}{m_D} - 1\right)^2 h \nu_{H_2}. \tag{29}$$

ψ_2 above refers to the wave function for the second excited state of the H_2 reference molecule. The results of these calculations going up to fourth order are tabulated in Table 1. The convergence of the perturbation series is remarkably good already in second order. It is however seen that the D_2 series converges less rapidly than the HD series. This is to be expected since the perturbation for D_2 is larger than it is for HD. The slower convergence of the D_2 series is magnified in the last column of Table 1 where the deviation from the law of the mean at the

	HD[b]	D_2	$(E_{HD} - E_{D_2}) - (E_{H_2} - E_{HD})$[c]
E_0^0	$\frac{1}{2}h\nu$	$\frac{1}{2}h\nu$	
E_0^1	$\frac{1}{2}h\nu$ (0.8750)	$\frac{1}{2}h\nu$ (0.7500)	$\frac{1}{2}h\nu$ (0.00000)
E_0^2	$\frac{1}{2}h\nu$ (0.8672)	$\frac{1}{2}h\nu$ (0.7188)	$\frac{1}{2}h\nu$ (0.01563)
E_0^3	$\frac{1}{2}h\nu$ (0.8662)	$\frac{1}{2}h\nu$ (0.7108)	$\frac{1}{2}h\nu$ (0.02158)
E_0^4	$\frac{1}{2}h\nu$ (0.8660)	$\frac{1}{2}h\nu$ (0.7084)	$\frac{1}{2}h\nu$ (0.02374)
Exact	$\frac{1}{2}h\nu$ (0.8660)	$\frac{1}{2}h\nu$ (0.7071)	$\frac{1}{2}h\nu$ (0.02494)

[a] The calculation was carried out with $m_H/m_D = 1/2$.
[b] ν refers to ν_{H_2}.
[c] This quantity was evaluated with the respective E_0 quantities appearing in the same row of the Table.

Table 1. The Calculation [a] of the Zero-point Energies of HD and D_2 with H_2 as the Reference Molecule.

	H_2[b]	D_2	$(E_{HD} - E_{D_2}) - (E_{H_2} - E_{HD})$[c]
E_0^0	$\frac{1}{2}h\nu$	$\frac{1}{2}h\nu$	
E_0^1	$\frac{1}{2}h\nu$ (1.1667)	$\frac{1}{2}h\nu$ (0.8333)	$\frac{1}{2}h\nu$ (0.00000)
E_0^2	$\frac{1}{2}h\nu$ (1.1528)	$\frac{1}{2}h\nu$ (0.8194)	$\frac{1}{2}h\nu$ (0.2778)
E_0^3	$\frac{1}{2}h\nu$ (1.1551)	$\frac{1}{2}h\nu$ (0.8171)	$\frac{1}{2}h\nu$ (0.02783)
E_0^4	$\frac{1}{2}h\nu$ (1.1546)	$\frac{1}{2}h\nu$ (0.8166)	$\frac{1}{2}h\nu$ (0.02874)
Exact	$\frac{1}{2}h\nu$ (1.1547)	$\frac{1}{2}h\nu$ (0.8165)	$\frac{1}{2}h\nu$ (0.02880)

[a] The calculation was carried out with $m_H/m_D = 1/2$.
[b] ν refers to ν_{HD}.
[c] This quantity was evaluated with the respective E_0 quantities appearing in the same row of the Table.

Table 2. The Calculation [a] of the Zero-point Energies of H_2 and D_2 with HD as the Reference Molecule.

various stages of perturbation may be compared with the corresponding exact value. To overcome this slower convergence of one molecule with respect to another, one may make a more symmetrical choice of reference molecule – i. e. one may choose HD as the reference molecule and now calculate the zero-point energies of D_2 and H_2. The results of such a calculation are shown in Table 2.

b) The NH diatomic molecule

An example of extremely rapid convergence of the perturbation is furnished by the calculation of the zero-point energy of $N^{15}H$ using $N^{14}H$ as the reference molecule in methodology B. One finds in units of $\frac{1}{2} h \nu_{N^{14}H}$, $E_0^1 = 0.9977777$, $E_0^2 = 0.9977753$ while $E_0(\text{exact}) = 0.9977753$.

c) The XY_2 molecule

The XY_2 molecule is considered as an example of a methodology A calculation. The molecule is taken to have a YXY angle of 90° and XY distance s. For the three internal coordinates the following are chosen: the two XY stretching coordinates R_1 and R_2 (with force constant k_1) and the YXY bend R_3 (with force constant k_δ). An interaction force constant k_{12} is assumed between R_1 and R_2. With the use of the rules for determining the values of G matrix elements one finds

$$2T = \left(\frac{1}{m_X} + \frac{1}{m_Y}\right)(p_1^2 + p_2^2) + \frac{1}{s^2}\left(\frac{2}{m_X} + \frac{2}{m_Y}\right) p_3^2 - \frac{1}{m_X}\frac{1}{s} 2(p_1 p_3 + p_2 p_3). \quad (30)$$

Also

$$2V = k_1(R_1^2 + R_2^2) + 2 k_{12} R_1 R_2 + k_\delta R_3^2. \quad (31)$$

With the use of methodology A, which has been described,

$$H_0 = \frac{1}{2}\left\{\left[\left(\frac{1}{m_X} + \frac{1}{m_Y}\right) p_1^2 + k_1 R_1^2\right] + \left[\left(\frac{1}{m_X} + \frac{1}{m_Y}\right) p_2^2 + k_1 R_2^2\right] + \left[\frac{1}{s^2}\left(\frac{2}{m_X} + \frac{2}{m_Y}\right) p_3^2 + k_\delta R_3^2\right]\right\}, \quad (32)$$

$$H_1 = -\frac{1}{m_X}\frac{1}{s}(p_1 p_3 + p_2 p_3) + k_{12} R_1 R_2. \quad (33)$$

Making use of eqs. (11) and (16), one obtains

$$E_0^0 = \frac{1}{2} h(2\nu_1 + \nu_3), \quad (34)$$

$$E_0^2 = E_0^0 - \frac{1}{4}\frac{1}{m_X^2}\left(\frac{1}{m_X} + \frac{1}{m_Y}\right)^{-2} \frac{h \nu_1 \nu_3}{\nu_1 + \nu_3} - \frac{k_{12}^2}{k_1^2}\frac{h\nu_1}{8} \quad (35)$$

where $\nu_1 = (2\pi)^{-1}\left[k_1\left(\frac{1}{m_X} + \frac{1}{m_Y}\right)\right]^{1/2}$,

$\nu_3 = (2\pi)^{-1}\left[k_\delta\left(\frac{2}{m_X} + \frac{2}{m_Y}\right)/s^2\right]^{1/2}$.

Take, as an example, the following reasonable parameters:

$m_X = 16$, $m_Y = 1$, $k_\delta/s^2 = 0.1\, k_1$, $k_{12} = -0.014\, k_1$.

Then, one obtains

$$E_0^0 = 1.2236\, h\nu_1, \quad E_0^2 = 1.2233\, h\nu_1$$

while an exact calculation of E_0 yields $1.2233\, h\nu_1$. It is seen that the zero-point energy is almost correctly given by E_0^0. The perturbation correction is very small. The methodology shows very clearly the contribution to the zero-point energy which one may expect from an interaction force constant k_{12}. For the case $m_Y = 2$ (isotopic substitution), one obtains $E_0^0 = 1.2236\, h\nu_1$ (with ν_1 properly defined for $m_Y = 2$) and $E_0^2 = 1.2226\, h\nu_1$. Thus most of the isotope effect here is contained in the difference in the E_0^0's.

d) The methane type molecule

The methane molecule presents a problem not encountered before – the redundant coordinate. The natural coordinates which one would use in a simple valence force potential function are four carbon-hydrogen stretching coordinates R_1, R_2, R_3, R_4 (with force constant k_1) and six HCH bending coordinates $\alpha_1, \ldots, \alpha_6$ (with force constant k_2).

Thus
$$2V = \sum_i^4 k_1 R_i^2 + \sum_j^6 k_2 \alpha_j^2. \quad (36)$$

However, there exists a relationship among the α's, $\Sigma\, \alpha_j = 0$, and this redundancy should be eliminated [6] before one proceeds with the present methodology. One can eleminate α_6, so that

$$2V = \sum_i^4 k_1 R_i^2 + 2\sum_j^5 k_2 \alpha_j^2 + 2\sum_{i<j}^5 k_2 \alpha_i \alpha_j. \quad (37)$$

[6] It is amusing to note that, if the redundancy is not removed and one works with ten coordinates here, E_0^0 is closer to E_0 (exact) than in the above calculation. However, the subsequent convergence is not as good.

The simple valence force potential now contains large off-diagonal force constants. One now continues in the standard manner with methodology A and writes the HAMILTONian in terms of the nine independent coordinates [7]. One obtains for CH_4 with $k^2/s^2 = 0.1\, k_1$ (s = carbon-hydrogen equilibrium separation), in units of $\frac{1}{2}h(1/2\pi)(k_1)^{1/2}$ – with $m_C = 12$, $m_H = 1$, $m_D = 2$)

$$E_0^0 = 7.497, \quad E_0^2 = 6.664, \quad E_0(\text{exact}) = 6.732.$$

Similarly for CD_4

$$E_0^0 = 5.527, \quad E_0^2 = 4.893, \quad E_0(\text{exact}) = 4.945.$$

For the isotope effect one obtains

$$\Delta_0^2 = E_0^2(CH_4) - E_0^2(CD_4) = 1.771,$$
$$\Delta_0(\text{exact}) = 1.787\,.$$

e) The non-planar vibrations of benzene

A number of calculations have been carried out for the zero-point energies of the out-of-plane vibrations of the isotopic benzenes. The force constants of MILLER and CRAWFORD [8] were employed. The non-planar coordinates consist of six γ's (bending of the CH bond out of the plane of the adjacent CCC linkage) and six δ's (torsion of a CCCC linkage). There are three redundancy conditions among the latter coordinates. Therefore only three δ type coordinates must be used in the final problem. The first calculations were carried out using symmetry coordinates [8] in conjunction with methodology A. Symmetry coordinates are linear combinations of the γ's and δ's which transform according to the group theoretical irreducible representations of the symmetry group of C_6H_6. They have the merit that many interaction G matrix elements are zero in C_6H_6 and C_6D_6. However in the lower symmetry C_6H_5D many of these zeroes no longer occur. Thus the perturbation H_1 will appear to be quite different for C_6H_5D when compared with C_6H_6 or C_6D_6. The results of the calculation are given in Table 3 A. The general convergence of the perturbation series is quite good. The convergence is somewhat slower than the examples previously given since the perturbation H_1 is relatively "large". The zero-point energy differences between C_6H_5D and C_6H_6 and also between C_6D_6 and C_6H_6 are quite well reproduced by the perturbation calculation in second order. While the unperturbed energies show a deviation from the law of the mean for isotopic zero-point energies (i. e. the linear dependence of zero-point energy on the number of equivalent H's replaced by D's, Section IV), this deviation is largely removed in second order, although it is still somewhat larger than the deviation obtained with the exact calculation.

	C_6H_6	C_6H_5D	C_6D_6
A. Methodology A with symmetry coordinates			
E_0^0	6.527	6.404	5.730
E_0^2	5.411	5.265	4.513
E_0 (exact)[a]	5.213	5.049	4.226
$E_0^2 - (E_0^2)_{C_6H_6}$		0.146	0.898
$E_0(\text{exact}) - E_0(\text{exact})_{C_6H_6}$		0.164	0.987
B. Methodology B with C_6H_6 as reference			
ΔE_0^1		0.143	0.858
$\Delta E_0^1 + \Delta E_0^2$		0.159	0.955
C. Methodology A with γ_i's			
E_0^0	6.533	6.403	5.753
E_0^2	5.527	5.380	4.642
$E_0^2 - (E_0^2)_{C_6H_6}$		0.147	0.885

[a] From the calculations in reference [10]. The constants of this reference were used on all these calculations.

Table 3. Zero-point Energies of Isotopic Benzenes (in arbitrary units).

A second calculation was carried out using methodology B with C_6H_6 as the reference molecule (this is probably not the best choice of reference molecule for these calculations). The results of this calculation are given in Table 3 B. It is seen that the ΔE's (perturbations to the zero-point energy in C_6H_6) converge excellently to the exact zero-point energy differences in second order perturbation. The first order perturbation energy obeys the law of the

[7] If one carries out incomplete isotopic substitution, say if one substitutes only one deuterium for one hydrogen, two different perturbation series can be obtained depending on whether one makes the substitution in the set of atoms 1, 2 or 3, 4 since these two sets do not appear equivalently in H_0 if α_6 is the angle involving hydrogen atoms 3 and 4. Even E_0^0 will be different for the two possible cases. Both perturbation series should, of course, converge to the same zero point energy. In order to calculate a reasonable isotope effect on the isotopic substitution at various stages of the perturbation it is recommended that one carry through the perturbation calculation for each of the two mentioned possibilities and that one average the E_0^k's so obtained at each step in the perturbation. Similar comments apply to the substitution of two or three deuteriums.

[8] F. A. MILLER and B. L. CRAWFORD JR., J. Chem. Phys. **14**, 282 [1946]. Set 1 was used.

mean exactly. The truth of this statement can be easily made obvious and will be discussed later. The law of the mean is still valid to very good approximation in second order perturbation theory too.

A third calculation was carried out. In this calculation methodology A was used. Instead of using symmetry coordinates as in the first calculation, the six coordinates γ_i were used together with the symmetry coordinate combinations of the δ_i. The latter coordinates do not involve motion of the hydrogens. This set of coordinates, while leading to somewhat slower convergence of the perturbation than that of the first calculation, is somewhat superior (at least conceptually) for calculating isotope effects on zero-points energies since it deals "symmetrically" with all H substitutions. Since the individual γ_i's involve only one hydrogen atom, the law of the mean will be automatically observed for the unperturbed energies. In the second order perturbation correction, cross terms (15) involving γ_i and the δ combinations will automatically follow the law of the mean – i. e. in C_6H_6 there are six hydrogen terms, in C_6H_5D there are five hydrogen terms and one deuterium term, in C_6D_6 there are six deuterium terms. Moreover, the unperturbed energies and the $\gamma_i - \delta$ terms are the same for various isotopic isomers – e. g. *o*-, *m*-, and *p*-$C_6H_4D_2$. The only terms in second order approximation which lead to deviations from the law of the mean are interaction terms involving γ_i and γ_j. Reference to (15) shows that such terms exist if there are g_{ij} elements coupling the respective momenta, and force constants f_{ij} coupling the two coordinates involving hydrogen motion. These terms happen to be quite small in this case and even they obey an approximate law of the mean. Thus the second order perturbation correction obeys law of the mean quite well. The calculation has shown that the deviation from the law of the mean in the series C_6H_6, C_6H_5D, *o*-$C_6H_4D_2$ is given by

$$[E_0^2(C_6H_6) - E_0^2(C_6H_5D)] - [E_0^2(C_6H_5D) - E_0^2(C_6H_4D_2)] = -0.46\ \mathrm{cm}^{-1}.$$

Moreover, the zero-point energy, in second order, of *o*-$C_6H_4D_2$ is $0.45\ \mathrm{cm}^{-1}$ lower than that for *m*-$C_6H_4D_2$. The results of some of the calculations are tabulated in Table 3 C. The convergence in the second order approximation is quite good, especially in regard to the isotope effect.

The general conclusion to be drawn from the above examples is that the perturbation series converges rather well. In general accuracies of better than 10% appear achievable by truncating the perturbation at second order. Isotope effects are also quite well calculated. The general approach is useful in gaining some feeling for the behavior of zero-point energies when parameters are varied.

IV. The Law of the Mean for Zero-Point Energy Changes on Isotopic Substitution

The approximate validity of the law of the mean for zero-point energies on isotopic substitution, i. e. that the zero-point energy of a molecule with a number of equivalent hydrogens is a linear function of the number of hydrogens replaced by deuterium, was empirically found by BERNSTEIN and PULLIN [9]. Further, explicit calculations of frequencies by solving secular equations to demonstrate this approximate validity are shown in the previous paper [10]. The isotopic law of the mean for the sum of the squares of the frequencies is, of course, given by the sum rule of DECIUS, WILSON and SVERDLOV [1]. The present method of calculating zero-point energies casts considerable light on the reasons behind the approximate validity of the law of the mean.

In methodology B, one calculates the isotope effect on the zero-point energies directly. For simplicity, the present argument will be made on the assumption that the reference molecule is isotopically unsubstituted (e. g. the all hydrogen compound). Designate the particular H_1 which corresponds to making an isotopic substitution at one of the n equivalent positions as $H_1(i)$. Since the positions are equivalent, the perturbation series for monosubstitution will be independent of which particular $H_1(i)$ is chosen. H_1 for the fully substituted compound is $\sum_i^n H_1(i)$. Thus the first order perturbation energy correction for the fully substituted compound is

$$\Delta E_0^1 = \int \Psi_0^* \sum H_1(i)\ \Psi_0\, d\tau = n \int \Psi_0^*\, H_1(i)\ \Psi_0\, d\tau. \tag{38}$$

[9] H. J. BERNSTEIN and A. D. E. PULLIN, J. Chem. Phys. **21**, 2188 [1953].

[10] J. BIGELEISEN, R. E. WESTON, JR., and M. WOLFSBERG, Z. Naturforschg. **18 a**, 210 [1963].

One thus finds that the first-order correction to the zero-point energy does follow the law of the mean. This has already been demonstrated for the cases of hydrogen and of benzene. Since ΔE_0^1 appears to reproduce the major portion of the zero-point energy isotope effect, it becomes reasonable to expect an approximate validity of the law of the mean for the zero-point energy isotope effect. The second order perturbation contribution for mono-substitution and complete substitution are respectively

$$\Delta E_0^2(\text{mono}) = \sum_{k \neq 0} (E_0^0 - E_k^0)^{-1} \cdot \left[\left| \int \Psi_0^* H_1(i) \, \Psi_k \, d\tau \right|^2 \right] \tag{39}$$

and

$$\Delta E_0^2(\text{full}) = \sum_{k \neq 0} (E_0^0 - E_k^0)^{-1} \left[n \left| \int \Psi_0^* H_1(i) \, \Psi_k \, d\tau \right|^2 + \sum_{\substack{i,j \\ i \neq j}} \int \Psi_0^* H_1(i) \, \Psi_k \, d\tau \int \Psi_k^* H_1(j) \, \Psi_0 \, d\tau \right]. \tag{40}$$

The first term in the brackets for the fully substituted compound does follow the law of the mean. It is the second term which gives rise to interaction between i and j and which leads to violations of the law of the mean. One can give rather complex mathematical arguments to derive upper quantitative limits for law of the mean violations. These will not be presented here. The maximum violations will occur in the case of the hydrogen molecule where the two isotopic positions are directly bonded to each other. Here

$$[E_0(\text{HD}) - E_0(\text{D}_2)]/[E_0(\text{H}_2) - E_0(\text{HD})] = 1.19 .$$

Some of the factors which affect the validity of the law of the mean may be more readily visualized within the framework of methodology A. If the coordinates can be so chosen that there are equivalent coordinates for each isotopic position (e. g. the last discussed benzene calculation) and if moreover each of the coordinates involves the motion of only one of the equivalent isotopic atoms, then the unperturbed energies will follow the law of the mean (e. g. Table 3 C). If it is not possible to make a reasonable choice of valence force coordinates such that coordinates involving motion of the equivalent atoms only involve these one at a time, then violations of the law of the mean will already occur for the unperturbed energies. Such coordinates may be YXY bending coordinates in the case of isotopic Y substitution. The violations will be of the same type as those found for the hydrogen molecule (which actually obeys the law of the mean pretty well). Such a violation of the law of the mean will always be in the direction of increasing zero-point energy difference between successive pairs of isotopic molecules as the number of heavy isotopic atoms increases. It is to be noted that relatively the largest deviations from the law of the mean will occur when such deviations must exist already in the E_0^0 values. If there is a redundancy problem in the coordinates involving motion of the set of equivalent atoms, the procedure outlined in footnote [7] should be followed. In such case, no additional problem will be encountered in the unperturbed energies. If one considers organic carbon-hydrogen systems with deuterium substitution in general, the main contributions to E_0^0 will arise from carbon-hydrogen stretching motions and these contributions will obey the law of the mean.

When no serious problem arises in the unperturbed energies, it is worthwhile to consider the second order perturbation term. As has already been pointed out in connection with the benzene calculations, many of the contributing terms to ΔE_0^2 follow the law of the mean. If one assumes that each of the isotopic coordinates involves the motion of only one of the equivalent atoms, then interaction terms between these coordinates and coordinates which do not involve motion of the atoms in the equivalent set lead to energy corrections which follow the law of the mean. The only terms leading to violations of the law of the mean are interaction terms (15) between the coordinates which involve the equivalent atoms. The latter terms between i and j are different depending on whether i and j are both unsubstituted, one substituted and one unsubstituted, or both substituted. These terms depend on the magnitude of g_{ij} and f_{ij} and one would expect that the magnitude of the terms in ΔE_0^2 leading to law of the mean violations would decrease as the equivalent atoms are further removed from one another. Similar types of arguments will apply to the consideration of higher order perturbation terms. The general statement to be made is that the law of the mean for isotope effects is expected to have greater validity as the equivalent atoms move further apart in such a way that the coupling between them through the G matrix and the F matrix decreases. However, even in the worst case the non-validity of the law of the mean will be no worse than in the aforementioned case $H_2 - HD - D_2$. The reader should be referred to

tables in the previous paper [10] for explicit calculations of zero-point energies by the secular equation method. Many of the effects mentioned here may be seen there.

V. Conclusions

Two quantum mechanical schemes for calculating zero-point energies of molecular systems have been proposed. The first of these does not require the solution of secular equations. The second scheme requires the solution of the secular equation for a reference molecule and then enables one to calculate isotope effects on the zero-point energies without solving further secular equations. Both of these schemes rest on the use of perturbation theory to calculate interactions. Rather good convergence is found for zero-point energies and isotope effects if the perturbation series are truncated at the second order expression. The approaches are useful for investigating the influence of many factors on zero-point energies [11], e. g. force constants, atomic masses, geometry, etc. In the present instance, the approaches have been employed to rationalize the approximate validity of the law of the mean for isotopic zero-point energy difference and to point out some of the factors which influence this validity.

[11] M. Wolfsberg, J. chim. phys., in press.

Mischungslücken in binären Systemen von Schwefelkohlenstoff und aliphatischen primären Alkoholen

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Herrn Professor Dr. Klaus Clusius *zum 60. Geburtstag gewidmet*

Flüssige Gemische aus Schwefelkohlenstoff und aliphatischen n-Alkoholen zeigen Mischungslücken. Gemessen wurden die Systeme CS_2+MeOH, CS_2+n-PrOH und CS_2+n-BuOH. Lage und Verlauf der Mischungslücken hängen von der Kettenlänge der Alkohol-Moleküle ab. Die kritischen Lösungstemperaturen $(kLT)_{max}$ sind durch eine parabolische Gleichung darstellbar.

1910 untersuchte Duclaux [1] in einer Mischungskältemaschine binäre Gemische, die Schwefelkohlenstoff enthielten, und beobachtete, daß bei manchen Flüssigkeitspaaren eine bestimmte Grenztemperatur nicht unterschritten werden konnte. Etwa 30 Jahre später konnte Clusius, anknüpfend an Duclauxs Experimente, zeigen, daß diese kritische Temperatur durch eine Entmischung der beiden Komponenten verursacht wurde.

Clusius und Ringer [2] haben die Mischungslücke des Systems $CS_2 + Me_2CO$ gemessen, während Clusius und Ulmke [3] die des Systems CS_2 + AcOMe untersuchten. In beiden Fällen lag die kritische Lösungstemperatur $(kLT)_{max}$ gerade unter -50 °C.

Andererseits zeigt der Schwefelkohlenstoff Mischungslücken auch mit MeOH bzw. mit EtOH, wie unter anderem McKelvy und Simpson [4] bewiesen haben: Diese fanden für das System CS_2 + MeOH eine $(kLT)_{max}$ von $+35{,}7$ °C, und für CS_2 + EtOH eine solche von $-24{,}4$ °C.

Die genannten Tatsachen führten uns zu der Annahme, daß eine Mischung von Schwefelkohlenstoff mit n-Alkoholen bzw. mit Ketonen oder Estern eine um so tiefere $(kLT)_{max}$ haben sollte, je mehr Kohlenstoffatome die zweite Komponente enthält.

Im folgenden werden nun die Ergebnisse einer Untersuchung binärer Gemische von Schwefelkohlenstoff mit einigen aliphatischen n-Alkoholen mitgeteilt.

Apparatur

Die benutzte Apparatur besteht im wesentlichen aus einem Kryostaten für das Temperaturgebiet zwischen $-100°$ und $+50$ °C, einer Anordnung zur Füllung der Meßpipetten und einer Einrichtung zur Messung der Entmischungstemperatur. Abb. 1 zeigt die Anlage schematisch.

[1] J. Duclaux, C. R. Acad. Sci., Paris **151**, 715 [1910].
[2] K. Clusius u. W. Ringer, Z. phys. Chem. **187**, 186 [1940].
[3] K. Clusius u. H. Ulmke, Z. phys. Chem. **189**, 331 [1941].
[4] E. C. McKelvy u. D. H. Simpson, J. Amer. Chem. Soc. **44**, 105 [1922].