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

By MAX WOLFSBERG

Chemistry Department, Brookhaven National Laboratory, Upton, New York, U.S.A.

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 literature1 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

\[
2V = \sum_{ij} f_{ij} q_i q_j, \quad (1)
\]

\[
2T = \sum_{ij} g_{ij} p_i p_j. \quad (2)
\]

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 Wilson1. The matrix \( F \) is independent of isotopic substitution while \( G \) does depend on isotopic substitution. The \( 3N - 6 \) normal frequencies \( \nu \) of the system are obtained by solving the secular equation involving the \( F \) and \( G \) matrices in one of its many alternative forms. One can also determine the transformation between normal coordinates \( Q \) and internal coordinates

\[
Q_i = \sum_r A_{iq} q_r. \quad (3)
\]

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

\[
2V = \sum_{ij} 4 \pi^2 \nu_i^2 Q_i^2, \quad 2T = \sum P_i^2 \quad (4)
\]

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

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is then

\[ H = T + V = \frac{1}{2} \left( \sum P_i^2 + \sum 4 \pi^2 v_i^2 Q_i^2 \right) \]

\[ = \frac{1}{2} \sum (P_i^2 + 4 \pi^2 v_i^2 Q_i^2). \]  (5)

Now \( P_i^2 + 4 \pi^2 v_i^2 Q_i^2 \) is the Hamiltonian of a harmonic oscillator which has quantum mechanical energy levels \( E_n = (n + 1/2) h v_i \) (\( n = 1, 2, 3, \ldots \)). 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 \( v_i \) 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

\[ E_0 = \frac{1}{2} \sum h v_i. \]  (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. 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,

\[ H = T + V = (1/2) \sum (g_{ij} p_i p_j + f_{ij} q_i q_j). \]  (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—Hamiltonian and \( H_1 \), which will be designated as the perturbation. Thus

\[ H = H_0 + H_1, \]  (8)

\[ H_0 = (1/2) \sum (g_{ij} p_i p_j + f_{ij} q_i q_j), \]  (9)

\[ H_1 = (1/2) \sum (g_{ij} p_i p_j + f_{ij} q_i q_j) \]  (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

\[ E_0^0 = \frac{1}{2} \sum h v_i = \frac{1}{2} \sum h v_i \]  (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 \( v_i \) 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. 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

\[ \Psi_0 = \psi_0(q_1) \psi_0(q_2) \cdots \psi_0(q_{3N-6}), \]  (12)

where the \( \psi_0^i \)'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

\[ \Delta E_0^1 = \int \cdots \int \Psi_0^* \left( g_{ij} p_i p_j + f_{ij} q_i q_j \right) \Psi_0 dq_1 \cdots dq_{3N-6} \]

\[ = \int \cdots \int \psi_0^* (q_i) p_i \psi_0 (q_i) dq_i \int \psi_0^* (q_i) p_j \psi_0 (q_j) dq_j \]

\[ + \int \cdots \int \psi_0^* (q_i) q_i \psi_0 (q_i) dq_i \int \psi_0^* (q_j) q_j \psi_0 (q_j) dq_j \]

\[ \times \prod_{s \neq i,j} \int \psi_0^* (q_s) \psi_0 (q_s) dq_s. \]  (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. Biegeluisen and P. Goldstein, Z. Naturforsch. 18a, 205 [1963], and J. Biegeluisen, R. E. Weston, Jr., and M. Wolfsberg, Z. Naturforsch. 18a, 210 [1963].

3 Perturbation methods may also be employed to find the \( v_i \)'s by the secular equation method. This approach has not been investigated here.

duct of integrals multiplying the term in brackets is, of course, just equal to unity since the wave functions \( \psi_0 \) are normalized. Integrals of the types in the brackets can be very easily evaluated and their values have also been tabulated in many publications. 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

\[
\Delta E_0^2 = \sum_{n=0} \frac{\left| f \cdots f \Psi_0^* H_1 \Psi_n dq_1 \cdots dq_{N-6} \right|^2}{E_0^0 - E_n^0}
\]

where \( \Psi_n \) refers to any excited state of the unperturbed Hamiltonian with corresponding energy \( E_n^0 \). Thus \( \Psi_n \) 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 \( E_0^0 - E_n^0 = -h v_i \). 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 \( \Psi_n \) contributes to \( \Delta E_0^2 \) 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

\[
-\frac{h}{4} \left[ \frac{g_{ij}}{(g_{ii} g_{jj})^{1/2}} + \frac{f_{ij}}{(f_{ii} f_{jj})^{1/2}} \right]^2 \frac{v_i v_j}{v_i + v_j}.
\]

(15)

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

\[
E_0^2 = \frac{1}{2} \sum_{i} \left( \frac{3}{2} \sum_{j} h v_j \right)
\]

\[
- \left( \frac{1}{4} \sum_{i<j} \left[ \frac{g_{ij}}{(g_{ii} g_{jj})^{1/2}} + \frac{f_{ij}}{(f_{ii} f_{jj})^{1/2}} \right]^2 \frac{h v_i v_j}{v_i + v_j} \right).
\]

(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

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

where

\[
H_0 = \frac{1}{2} \sum_{i,j} (g_{ij} p_i p_j + f_{ij} q_i q_j) = \frac{1}{2} \sum_i (P_i^2 + 4 \pi^2 r_i^2 Q_i^2)
\]

and

\[
H_1 = \frac{1}{2} \sum_{i,j} (g'_{ij} - g_{ij}) p_i p_j = \frac{1}{2} \sum_{i,j} (g'_{ij} - g_{ij}) A_{ir} A_{js} P_r P_s.
\]

(17)

(18)

(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 \( v_i \) 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-

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ordinate \( r \) with corresponding conjugate momentum \( p_r \) is taken to be \( k \) so that
\[
2V = kr^2. \tag{20}
\]
The kinetic energy expressions for the three molecules are found remembering that \( g_{rr} = \frac{1}{m_1} + \frac{1}{m_2}, \)
\[
2T_{H_2} = \frac{2}{m_H} p_r^2, \quad 2T_{HD} = \left( \frac{1}{m_H} + \frac{1}{m_D} \right) p_r^2, \tag{21}
\]
\[
2T_{D_2} = \frac{2}{m_D} p_r^2
\]
where \( m \) refers to the relevant atomic mass. The zero-point energy for the reference molecule, \( H_2 \), is given by
\[
E_0 = \frac{1}{2} \hbar \left( \frac{2}{m_H} \right)^{1/2} = \frac{1}{2} \hbar \nu_{H_2}. \tag{22}
\]
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
\[
(H_1)_{HD} = H_{HD} - H_{H_2} = \frac{1}{2} \left( \frac{1}{m_D} - \frac{1}{m_H} \right) p_r^2 = \frac{1}{2} \left( \frac{m_H}{m_D} - 1 \right) p^2 \tag{24}
\]
and
\[
(H_1)_{D_2} = H_{D_2} - H_{H_2} = \frac{1}{2} \left( \frac{1}{m_D} - \frac{1}{m_H} \right) p_r^2 = \frac{1}{2} \left( \frac{m_H}{m_D} - 1 \right) P^2. \tag{25}
\]
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
\[
(\Delta E_0^1)_{HD} = \frac{1}{4} \left( \frac{m_H}{m_D} - 1 \right) \int \psi_0^2 P^2 \psi_0 \, dQ
\]
\[
= \frac{1}{8} \left( \frac{m_H}{m_D} - 1 \right) \hbar \nu_{H_2}. \tag{26}
\]
and similarly
\[
(\Delta E_0^1)_{D_2} = \frac{1}{4} \left( \frac{m_H}{m_D} - 1 \right) \hbar \nu_{H_2}. \tag{27}
\]
In second order perturbation
\[
(\Delta E_0^2)_{HD} = \frac{1}{16} \left( \frac{m_H}{m_D} - 1 \right)^2 \left( \frac{1}{-2 \hbar \nu} \right) \int \psi_0^2 P^2 \psi_2 \, dQ
\]
\[
= - \frac{1}{64} \left( \frac{m_H}{m_D} - 1 \right)^2 \hbar \nu_{H_2}. \tag{28}
\]
and
\[
(\Delta E_0^2)_{D_2} = - \frac{1}{16} \left( \frac{m_H}{m_D} - 1 \right)^2 \hbar \nu_{H_2}. \tag{29}
\]
\( \psi_2 \) 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

<table>
<thead>
<tr>
<th>( H_2 )</th>
<th>( D_2 )</th>
<th>( (E_{HD} - E_{D_2}) - (E_{H_2} - E_{HD}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_0^0 )</td>
<td>( \frac{1}{2} \hbar \nu )</td>
<td>( \frac{1}{2} \hbar \nu )</td>
</tr>
<tr>
<td>( E_0^1 )</td>
<td>( \frac{1}{2} \hbar \nu (0.8750) )</td>
<td>( \frac{1}{2} \hbar \nu (0.7500) )</td>
</tr>
<tr>
<td>( E_0^2 )</td>
<td>( \frac{1}{2} \hbar \nu (0.8672) )</td>
<td>( \frac{1}{2} \hbar \nu (0.7188) )</td>
</tr>
<tr>
<td>( E_0^3 )</td>
<td>( \frac{1}{2} \hbar \nu (0.8662) )</td>
<td>( \frac{1}{2} \hbar \nu (0.7108) )</td>
</tr>
<tr>
<td>( E_0^4 )</td>
<td>( \frac{1}{2} \hbar \nu (0.8660) )</td>
<td>( \frac{1}{2} \hbar \nu (0.7084) )</td>
</tr>
<tr>
<td>Exact</td>
<td>( \frac{1}{2} \hbar \nu (0.8660) )</td>
<td>( \frac{1}{2} \hbar \nu (0.7071) )</td>
</tr>
</tbody>
</table>

\( a \) The calculation was carried out with \( m_{H_D} = 1/2. \)

<table>
<thead>
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</tr>
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<tbody>
<tr>
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<td>( \frac{1}{2} \hbar \nu )</td>
<td>( \frac{1}{2} \hbar \nu )</td>
</tr>
<tr>
<td>( E_0^1 )</td>
<td>( \frac{1}{2} \hbar \nu (1.1667) )</td>
<td>( \frac{1}{2} \hbar \nu (0.8333) )</td>
</tr>
<tr>
<td>( E_0^2 )</td>
<td>( \frac{1}{2} \hbar \nu (1.1528) )</td>
<td>( \frac{1}{2} \hbar \nu (0.8194) )</td>
</tr>
<tr>
<td>( E_0^3 )</td>
<td>( \frac{1}{2} \hbar \nu (1.1551) )</td>
<td>( \frac{1}{2} \hbar \nu (0.8171) )</td>
</tr>
<tr>
<td>( E_0^4 )</td>
<td>( \frac{1}{2} \hbar \nu (1.1546) )</td>
<td>( \frac{1}{2} \hbar \nu (0.8166) )</td>
</tr>
<tr>
<td>Exact</td>
<td>( \frac{1}{2} \hbar \nu (1.1547) )</td>
<td>( \frac{1}{2} \hbar \nu (0.8165) )</td>
</tr>
</tbody>
</table>
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 D₂ and H₂. 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 N¹⁸H using N¹⁴H as the reference molecule in methodology B. One finds in units of \( \frac{1}{2} h v_{\text{rot}} \), \( E_{0} = 0.9977777 \), \( E_{0} = 0.9977775 \) while \( E_{0}(\text{exact}) = 0.9977753 \).

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

\[ E_{0} = \frac{1}{2} h (2 v_{1} + v_{3}), \]
\[ E_{0} = \frac{1}{4} \frac{1}{m_{x}} \left[ \frac{1}{m_{x}} + \frac{1}{m_{y}} \right] v_{1}^{2} + k_{2} v_{1}^{2} + k_{3} v_{2}^{2} \]
\[ v_{3} = (2 \pi)^{-1} \left( k_{3} \left( \frac{1}{m_{x}} + \frac{1}{m_{y}} \right) + k_{3} \frac{s^{2}}{2} \right)^{1/2}. \]

Then, one obtains

\[ E_{0} = 1.2236 h v_{1}, \quad E_{0} = 1.2233 h v_{1} \]

while an exact calculation of \( E_{0} \) yields \( 1.2233 h v_{1} \). It is seen that the zero-point energy is almost correctly given by \( E_{0} \). 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

\[ E_{0} = 1.2236 h v_{1} \]

with \( v_{1} \) properly defined for \( m_{y} = 2 \) and \( E_{0} = 1.2226 h v_{1} \). Thus most of the isotope effect here is contained in the difference in the \( E_{0} \)’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

\[ 2 V = \sum_{i}^{4} k_{1} R_{i}^{2} + \sum_{j}^{6} k_{2} \alpha_{j}^{2}. \]

However, there exists a relationship among the \( \alpha \)'s, \( \sum \alpha_{j} = 0 \), and this redundancy should be eliminated before one proceeds with the present methodology. One can eliminate \( \alpha_{6} \) so that

\[ 2 V = \sum_{i}^{4} k_{1} R_{i}^{2} + 2 \sum_{k}^{5} k_{2} \alpha_{j}^{2} + 2 \sum_{k}^{5} k_{2} \alpha_{j} \alpha_{j}. \]
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 \(\text{CH}_4\) with \(k_1^2 s^2 = 0.1 \ k_1\) \((s = \text{carbon-hydrogen equilibrium separation})\), in units of \(\frac{1}{2} \hbar (1/2 \pi) (k_1)^{1/2}\) 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 \(\text{CD}_4\)

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

For the isotope effect one obtains

\[
A_0^2 = E_0^2(\text{CH}_4) - E_0^2(\text{CD}_4) = 1.771, \quad A_0\text{ (exact)} = 1.787.
\]

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 \(\gamma\)'s (bending of the CH bond out of the plane of the adjacent CCC linkage) and six \(\delta\)'s (torsion of a CCC linkage). There are three redundancy conditions among the latter coordinates. Therefore only three \(\delta\) 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 \(\gamma\)'s and \(\delta\)'s which transform according to the group theoretical irreducible representations of the symmetry group of \(\text{C}_6\text{H}_6\). They have the merit that many interaction \(G\) matrix elements are zero in \(\text{C}_6\text{H}_6\) and \(\text{C}_6\text{D}_6\). However in the lower symmetry \(\text{C}_6\text{H}_5\text{D}\) many of these zeroes no longer occur. Thus the perturbation \(H_1\) will appear to be quite different for \(\text{C}_6\text{H}_5\text{D}\) when compared with \(\text{C}_6\text{H}_6\) or \(\text{C}_6\text{D}_6\). 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 \(\text{C}_6\text{H}_5\text{D}\) and \(\text{C}_6\text{H}_6\) and also between \(\text{C}_6\text{D}_6\) and \(\text{C}_6\text{H}_6\) 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.

![Table 3. Zero-point Energies of Isotopic Benzenes (in arbitrary units).](image)

\(^7\) 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 \(H_5\) if \(\alpha_4\) 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 \( \gamma_i \) were used together with the symmetry coordinate combinations of the \( \delta_i \). 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 \( \gamma_i \)’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 \( \gamma_i \) and the \( \delta \) combinations will automatically follow the law of the mean — i.e. in \( C_6H_6 \) there are six hydrogen terms, in \( C_6H_4D \) 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. \( \alpha-, \ m-, \text{ and } p-C_6H_4D_2 \). The only terms in second order approximation which lead to deviations from the law of the mean are interaction terms involving \( \gamma_i \) and \( \gamma_j \). 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

\[
\begin{align*}
[E_0^0(C_6H_6) - E_0^0(C_6H_5D)] - [E_0^0(C_6H_5D) - E_0^0(C_6H_4D_2)] = -0.46 \text{ cm}^{-1}.
\end{align*}
\]

Moreover, the zero-point energy, in second order, of \( o-C_6H_4D_2 \) is 0.45 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 Dectus, Wilson and Sverdlov. 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 \( \Sigma_i H_1(i) \). Thus the first order perturbation energy correction for the fully substituted compound is

\[
\Delta E_0^1 = \int \Psi_0^* \sum H_1(i) \Psi_0 \, d\tau = n \int \Psi_0^* H_1(i) \Psi_0 \, d\tau.
\]


\(^{10}\) J. Bigeleisen, R. E. Weston, Jr., and M. Wolfsberg, Z. Naturforsch. 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 $\Delta E_0^1$ 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

$$\Delta E_0^2(\text{mono}) = \sum_{k \neq 0} (E_0^0 - E_k^0)^{-1} [\int \Psi_0^* H_1(i) \Psi_k \, dr]^2$$

and

$$\Delta E_0^2(\text{full}) = \sum_{k \neq 0} (E_0^0 - E_k^0)^{-1} \left[ \int \Psi_0^* H_1(i) \Psi_k \, dr \right]^2 + \sum_{i \neq j} \int \Psi_j^* H_1(i) \Psi_k \, dr \int \Psi_k^* H_1(j) \Psi_0 \, dr$$

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

$$[E_0^0(\text{HD}) - E_0^0(\text{D}_2)]/[E_0^0(\text{H}_2) - E_0^0(\text{HD})] = 1.19.$$  

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? 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 $\Delta E_0^2$ 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 $\Delta E_0^2$ 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 $\text{H}_2 - \text{HD} - \text{D}_2$. The reader should be referred to
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, 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 isotope zero-point energy difference and to point out some of the factors which influence this validity.

Mischungslücken in binären Systemen von Schwefelkohlenstoff und aliphatischen primären Alkoholen

Von Paolo Franzosini

Aus dem Physikalisch-Chemischen Institut der Universität Pavia

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.


Clusius und Ringer$^2$ haben die Mischungslücke des Systems CS$_2$+Me$_2$CO gemessen, während Clusius und Ulmke$^3$ die des Systems CS$_2$+AcOMe untersuchten. In beiden Fällen lag die kritische Lösungstemperatur ($kLT$)$_{max}$ gerade unter $-50 \, ^\circ C$.

Andererseits zeigt der Schwefelkohlenstoff aschungslücken 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 $+35,7 \, ^\circ C$, und für CS$_2$+EtOH eine solche von $-24,4 \, ^\circ C$.

Die genannten Tatsachen führten uns zu der Annahme, daß eine Mischung von Schwefelkohlenstoff mit n-Alkoholen bzw. mit Ketonen oder Estern eine um so tieferere ($kLT$)$_{max}$ 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 $-100 \, ^\circ C$ und $+50 \, ^\circ C$, einer Anordnung zur Füllung der Meßpipetten und einer Einrichtung zur Messung der Entmischungstemperatur. Abb. 1 zeigt die Anlage schematisch.

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