

Normal boron trichloride consists of about 80% $^{11}\text{BCl}_3$ and 20% $^{10}\text{BCl}_3$. The boron isotope effect on the ν_3 vibration is fairly large ($\sim 40\text{ cm}^{-1}$) and is well understood.² For each boron isotope the natural abundances of the chlorine isotopes are 42.2% B^{35}Cl_3 , 42.2% $\text{B}^{35}\text{Cl}_2^{37}\text{Cl}$, 14.1% $\text{B}^{35}\text{Cl}^{37}\text{Cl}_2$ and 1.6% B^{37}Cl_3 . Substitution of ^{37}Cl for ^{35}Cl not only tends to lower the vibrational frequency but reduces the symmetry, which leads to a splitting of degeneracies. The vibrational frequencies of the various isotopic species of BCl_3 were calculated from a general force field which was derived from the boron isotopic frequency data and the Coriolis coupling constants. The use of these zeta constants which were obtained by infrared gas-phase band-contour measurements uniquely specifies the force constants for the E vibrational mode.¹ The calculated separations of the components of BCl_3 due to isotopic splittings are given in Table I. The expected relative intensities can be estimated by assuming that each component has the same inherent absorptivity and has a concentration determined by the natural abundance of ^{37}Cl (24.6%). Indirect evidence for such an approach was obtained in the case of CCl_4 .³

The matrix spectrum is shown in Fig. 1. With a thin film, ν_3 of $^{11}\text{BCl}_3$ is split into four components and appears similar to ν_3 of $^{10}\text{BCl}_3$. The observed separations are given in Table I together with the calculated shifts. The accidental degeneracy of $\nu_{3a'}$ and ν_3 produces the strongest band in the spectrum with a relative intensity of 9 followed by bands of relative intensity 1, 3, and 1. $\nu_{3''}$ due to its low intensity and near-accidental degeneracy with ν_3'' tends to be obscured. The excellent agreement between the calculated and observed shifts lends support to the force field used.

The fact that the observed effect does not change either with temperature (14° or 20°K) or with concentration, coupled with the excellent agreement between

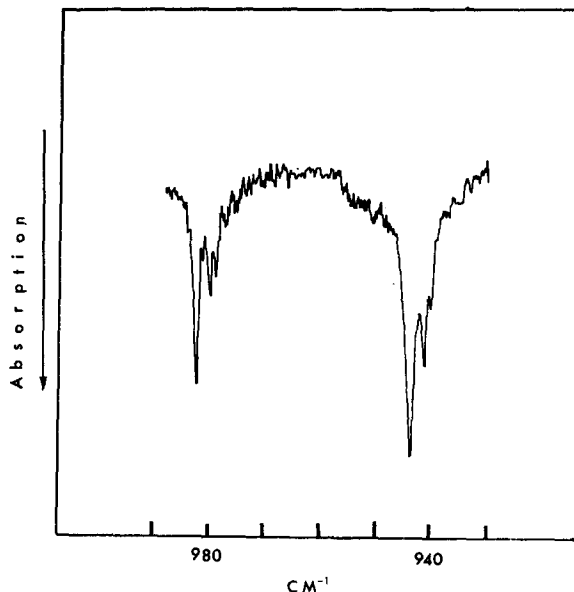


FIG. 1. ν_3 of matrix-isolated BCl_3 , 1/200 Ar, 14°K .

the computed and observed spectra rules out matrix effects as a cause of the splitting. The spectra were recorded using a prism-grating spectrophotometer with a conventional low-temperature Dewar.

¹ I. W. Levin and S. Abramowitz, *J. Chem. Phys.* **43**, 4213 (1965).

² G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), Vol. 2.

³ S. Abramowitz and R. P. Bauman, *J. Chem. Phys.* **39**, 2757 (1963).

Energy Differences and Parr's Integral Hellmann-Feynman Theorem

HARRIS J. SILVERSTONE

*Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland*

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TO calculate internal-rotation barriers, equilibrium nuclear geometries, and vibrational force constants, one must compare total molecular energies (in the Born-Oppenheimer approximation) for different nuclear configurations (X and Y): $\Delta W \equiv E_X - E_Y$. For approximate energies (E_X^a , E_Y^a) the errors $|E_X - E_X^a|$ and $|E_Y - E_Y^a|$ are often an order of magnitude greater than ΔW . Thus, to use $\Delta W \approx \Delta W_{\text{ed}}^a \equiv E_X^a - E_Y^a$ needs careful justification.¹ [The "ed" denotes "energy-difference" formula.]

Another approach to conformational energy differences is the integral Hellmann-Feynman theorem discovered independently by Parr² and Richardson and Pack³: $\Delta W = \Delta W_{\text{PIHFT}} \equiv \langle \psi_X | H_X - H_Y | \psi_Y \rangle / \langle \psi_X | \psi_Y \rangle$. [H_X , H_Y , ψ_X and ψ_Y are the electronic Hamiltonians (including internuclear repulsions) and the exact elec-

TABLE I. Isotopic splitting of the ν_3 fundamental.

Species	Abundance ^a (%)	Vibration	Relative Intensity (calculated)	Calculated Shift	Observed Shift
$^{10}\text{B}^{35}\text{Cl}_3$	42.2	ν_3	9	0	0
$^{10}\text{B}^{35}\text{Cl}_2^{37}\text{Cl}$	42.2	$\nu_{3a'}$		0	0
$^{10}\text{B}^{37}\text{Cl}_2^{35}\text{Cl}$	14.1	$\nu_{3b'}$	3	3.2	2.8
		$\nu_{3a''}$	1	1.6	1.4
		$\nu_{3b''}$	1	4.8	3.9
$^{10}\text{B}^{37}\text{Cl}_3$	1.6	$\nu_{3''}$	0.2	4.8	...
$^{11}\text{B}^{35}\text{Cl}_3$	42.2	ν_3	9	0	0
$^{11}\text{B}^{35}\text{Cl}_2^{37}\text{Cl}$	42.2	$\nu_{3a'}$		0	0
$^{11}\text{B}^{37}\text{Cl}_2^{35}\text{Cl}$	14.1	$\nu_{3b'}$	3	3.4	2.7
		$\nu_{3a''}$	1	1.7	1.4
		$\nu_{3b''}$	1	4.8	4.1
$^{11}\text{B}^{37}\text{Cl}_3$	1.6	$\nu_{3''}$	0.2	5.1	...

^a The ^{10}B and ^{11}B isotopes are treated separately since the boron isotope shift is much greater ($\sim 40\text{ cm}^{-1}$) than the chlorine isotope effect.

tronic wavefunctions. (PIHFT is Parr's integral Hellmann-Feynman theorem.)] The following analysis by Wyatt and Parr^{4,5} shows that the PIHFT should be reliable for approximate (but reasonable) wavefunctions. Denote the difference between the exact and approximate wavefunctions by $\lambda\delta_X = \psi_X - \psi_X^a$ and $\lambda\delta_Y = \psi_Y - \psi_Y^a$. [Choose the parameter λ so that $\langle \delta_X | \delta_X \rangle \sim 1 \sim \langle \delta_Y | \delta_Y \rangle$.] With $\Delta H = H_X - H_Y$, one finds

$$\begin{aligned} \Delta W_{\text{PIHFT}}^a &= \Delta W_{\text{PIHFT}} \\ &+ \lambda[\Delta W_{\text{PIHFT}}^a(\langle \delta_X | \psi_Y^a \rangle + \langle \psi_X^a | \delta_Y \rangle) \\ &- \langle \delta_X | \Delta H | \psi_Y^a \rangle - \langle \psi_X^a | \Delta H | \delta_Y \rangle] / \langle \psi_X^a | \psi_Y^a \rangle + O(\lambda^2). \end{aligned} \quad (1)$$

The error in $\Delta W_{\text{PIHFT}}^a$ is of the order of $\lambda \times \Delta H$. For reasonable approximate wavefunctions, both $\lambda < 1$ and $|\langle \delta_{X,Y} | \Delta H | \psi_{Y,X}^a \rangle| \lesssim \Delta W_{\text{PIHFT}}^a$.

Because of the extremum property of the energy, $\Delta W_{\text{ed}} - \Delta W_{\text{ed}}^a$ is of the order of λ^2 . Since, in general, there is no explicit relationship between ψ_X^a and ψ_Y^a (in terms of ΔH), the coefficient of λ^2 can not easily be expressed in powers of ΔH , nor can the error $\Delta W_{\text{ed}} - \Delta W_{\text{ed}}^a$. [The referee has emphasized, however, that (at least) when the conformational change is infinitesimal, the coefficient will be of the order of ΔH . Note that in the ethane barrier case, the change is not infinitesimal. Indeed, one finds⁵ that $\langle \psi_X^a | \psi_Y^a \rangle \sim 0.5$.] Nevertheless, whenever $\Delta W_{\text{ed}}^a \approx \Delta W_{\text{PIHFT}}^a$, the ed-formula error is at least as small as $\lambda \times \Delta H$, and both values are thus reasonable estimates of ΔW . (Which estimate is more accurate depends upon the nature of the approximate wavefunctions.) Thus it is useful to know when $\Delta E_{\text{ed}}^a \approx \Delta W_{\text{PIHFT}}^a$.

The purpose of this note is to show that in the Hartree-Fock approximation, if the localized orbitals⁶ did not change, then $\Delta W_{\text{ed}}^{\text{HF}}$ would equal $\Delta W_{\text{PIHFT}}^{\text{HF}}$ for a large class of molecules. Thus, $\Delta W_{\text{ed}}^{\text{HF}} - \Delta W_{\text{PIHFT}}^{\text{HF}}$ is a measure of changes in localized orbitals. In addition, for another type of approximate wavefunction, ΔW_{ed}^a and $\Delta W_{\text{PIHFT}}^a$ will always be equal.

We find for the difference of the two formulas, using the well-known properties of Hartree-Fock functions,

$$\begin{aligned} &\langle \psi_X^{\text{HF}} | H_X - H_Y | \psi_Y^{\text{HF}} \rangle / \langle \psi_X^{\text{HF}} | \psi_Y^{\text{HF}} \rangle \\ &- \langle \psi_X^{\text{HF}} | H_X | \psi_X^{\text{HF}} \rangle + \langle \psi_Y^{\text{HF}} | H_Y | \psi_Y^{\text{HF}} \rangle \\ &= \Delta W_{\text{PIHFT}}^{\text{HF}} - \Delta W_{\text{ed}}^{\text{HF}} \\ &= - \langle \psi_X^{\text{HF}} | \sum_{i=1}^N \sum_{j=1}^N [J_{i^X}(j) - K_{i^X}(j) - J_{i^Y}(j) + K_{i^Y}(j)] \\ &\quad \times \frac{|\psi_Y^{\text{HF}}\rangle}{\langle \psi_X^{\text{HF}} | \psi_Y^{\text{HF}} \rangle} + \sum_{i < j}^N (J_{ij^X} - K_{ij^X} - J_{ij^Y} + K_{ij^Y}). \end{aligned} \quad (2)$$

Here $J_i(j)$ and $K_i(j)$ are the Coulomb and exchange operators of Spin Orbital i acting on Electron j , and J_{ij} and K_{ij} are the Coulomb and exchange integrals. The superscript X and Y indicates which Hartree-Fock

determinant the spin orbitals are from. There are N -spin orbitals from each.

Suppose that X and Y differ by an internal rotation about, or by the bending or stretching of one bond. More precisely, divide the molecule into two parts— U , which is unmoved, and M , which is moved as a rigid unit to get X from Y . Make the hypothesis that in going from X to Y the localized orbitals^{6,7} of U are invariant, and the localized orbitals of M move along with the atoms and bonds (perfect following), but are otherwise unchanged (frozen). Equation (2) holds for localized orbitals. For localized spin orbitals ϕ_u belonging to U ($\phi_u^X = \phi_u^Y = \phi_u$),

$$J_u^X(j) - J_u^Y(j) = 0 = K_u^X(j) - K_u^Y(j),$$

and

$$J_{uu^X} - J_{uu^Y} = 0 = K_{uu^X} - K_{uu^Y}.$$

For spin orbitals $\phi_m^{X,Y}$, $\phi_{m'}^{X,Y}$ belonging to M ,

$$J_{mm^X} - J_{mm^Y} = 0 = K_{mm^X} - K_{mm^Y},$$

and

$$\langle \phi_u | J_m^X(u) - K_m^X(u) | \phi_u \rangle = J_{mu^X} - K_{mu^X}$$

(likewise for Y). These extensive cancellations reduce Eq. (2) to

$$\begin{aligned} \Delta W_{\text{PIHFT}}^{\text{HF}} - \Delta W_{\text{ed}}^{\text{HF}} &\rightarrow - \langle \psi_{XM} | \\ &\times \sum_m \sum_{m'} [J_m^X(m') - K_m^X(m') - J_m^Y(m') + K_m^Y(m')] \\ &\quad \times |\psi_{YM}\rangle / \langle \psi_{XM} | \psi_{YM} \rangle, \end{aligned} \quad (3)$$

where ψ_{XM} and ψ_{YM} are Slater determinants of the localized spin orbitals of the moved part of the molecule, and m and m' each enumerate these spin orbitals.

One assumption about the M group itself makes Eq. (3) vanish: If there is a plane of symmetry which takes ψ_{XM} into ψ_{YM} , then $\Delta W_{\text{PIHFT}}^{\text{HF}} - \Delta W_{\text{ed}}^{\text{HF}} = 0$ (perfect following frozen localized orbitals; plane of symmetry).

As an example, the calculated ethane internal-rotation barrier would be the same for both formulas with Hartree-Fock wavefunctions if the localized orbitals were unchanged. The Pitzer-Lipscomb¹ minimal-basis-set Hartree-Fock calculation gives $\Delta W_{\text{ed}}^{\text{HF}} = -49\,564.46 + 49\,567.74$ kcal/mole = 3.3 kcal/mole. With the same wavefunction,⁵ $\Delta W_{\text{PIHFT}}^{\text{HF}} = 2.3$ kcal/mole. The difference, -1.0 kcal/mole, indicates that the localized orbitals change slightly from eclipsed to staggered ethane, as direct examination of the localized orbitals shows.⁸ Nevertheless, that $\Delta W_{\text{ed}}^{\text{HF}} \approx \Delta W_{\text{PIHFT}}^{\text{HF}}$ adds credence to both values. (Note, however, that the minimal-basis-set orbitals are not exact Hartree-Fock orbitals.)

If the M 's in the X and Y configurations cannot be related by a plane of symmetry (as in internal rotation or vibration of a -CClFBr group), then Eq. (3) $\neq 0$, but a modified statement can be proved. Let Y_1 be one conformation and Y_2 a second obtained from X by moving M in the opposite sense from Y_1 (but by

the same amount). Then the sum, $\Delta W^{\text{HF}}(X \rightarrow Y_1) + \Delta W^{\text{HF}}(X \rightarrow Y_2)$, calculated by either the PIHFT or ed method, is the same (with perfect following frozen localized orbitals). This result would be useful when X is an equilibrium configuration.

A case, first noted by Epstein,⁹ for which $\Delta W_{\text{ed}}^a \equiv \Delta W_{\text{PIHFT}}^a$, is when ψ_X^a and ψ_Y^a are each the best (in energy) linear combinations of the same n (N -electron) basis functions. Within the n -dimensional subspace spanned by the basis, ψ_X^a and ψ_Y^a are exact eigenvectors of the $n \times n$ matrices of H_X and H_Y . For exact wavefunctions, the formulas are equivalent.^{2,3}

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⁹ R. G. Parr (private communication); S. Epstein, A. C. Hurley, R. E. Wyatt, and R. G. Parr (to be published).

Transport Coefficients for Systems with Steep Intermolecular Potentials*

R. G. STORER†

*Courant Institute of Mathematical Sciences, New York University
New York, New York*

AND

H. L. FRISCH

Bell Telephone Laboratories, Murray Hill, New Jersey

AND

*Courant Institute of Mathematical Sciences, New York University,
New York, New York*

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RECENTLY Frisch and Berne¹ (whose notation we follow) have obtained a formal high-temperature perturbation expansion of the thermal transport coefficients of a fluid starting with the Kubo-Green correlation-function expressions and choosing the rigid-sphere fluid as the reference system. We extend the thermodynamic perturbation of the Kubo-Green formulation of the transport coefficients by considering here the expansion of the self-diffusion coefficient D in powers of n^{-1} where n is a measure of the steepness of the intermolecular potential. Rowlinson² has previously given the corresponding expansion in n^{-1} of the equilibrium properties.

Let $\phi(\mathbf{r}, n)$ be the intermolecular potential for the

molecular separation \mathbf{r} with $\lim_{n \rightarrow \infty} \phi(\mathbf{r}, n)$ the hard-sphere potential with diameter a . We want an expansion in n^{-1} of D of the form

$$D = D_0 + n^{-1}D_1 + \dots, \quad (1)$$

with D_0 the self-diffusion coefficient of the hard-sphere fluid and

$$D_1 = \lim_{n \rightarrow \infty} \partial D / \partial (n^{-1}). \quad (2)$$

Starting from the Kubo-Green expression [Eq. (3.1) of Ref. 1],

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}_1(0) \cdot \mathbf{v}_1(t) \rangle, \quad (3)$$

and letting

$$\mathbf{F}_1 = -\frac{\partial}{\partial \mathbf{x}_{1j \neq 1}} \sum_{j=1}^N \phi(\mathbf{r}_{ij}), \quad (4)$$

one finds ($\beta = 1/kT$)

$$\begin{aligned} \frac{\partial D}{\partial n^{-1}} &= -\frac{1}{3} \int_0^\infty dt \left\langle \mathbf{v}_1(0) \cdot \mathbf{v}_1(t) \beta \right. \\ &\quad \times \sum_{i < j} \left[\frac{\partial u[\mathbf{r}_{ij}(0)]}{\partial n^{-1}} - \left\langle \frac{\partial u[\mathbf{r}_{ij}(0)]}{\partial n^{-1}} \right\rangle \right] \Bigg\rangle \\ &\quad + \frac{1}{3} \int_0^\infty dt \left\langle \mathbf{v}_1(0) \cdot \frac{\partial \mathbf{v}_1(t)}{\partial n^{-1}} \right\rangle \\ &= -\frac{1}{3} \int_0^\infty dt \left\langle \mathbf{v}_1(0) \cdot \mathbf{v}_1(t) \beta \right. \\ &\quad \times \sum_{i < j} \left[\frac{\partial u[\mathbf{r}_{ij}(0)]}{\partial n^{-1}} - \left\langle \frac{\partial u[\mathbf{r}_{ij}(0)]}{\partial n^{-1}} \right\rangle \right] \Bigg\rangle \\ &\quad + \frac{1}{3} \int_0^\infty dt \left\langle m^{-1} \frac{\partial \mathbf{F}_1(0)}{\partial n^{-1}} \cdot [\mathbf{x}_1(t) - \mathbf{x}_1(0)] \right\rangle, \quad (5) \end{aligned}$$

where the last equality is obtained by use of microscopic reversibility as in Sec. 3 of Ref. 1. The limits of the derivatives of ϕ and \mathbf{F}_1 with respect to n^{-1} as $n \rightarrow \infty$ only exist in the sense of distributions. To obtain the relevant limiting expressions we write, e.g., the last term of (5) as

$$\begin{aligned} &-\frac{1}{3} \int_0^\infty dt \int_0^\infty dr 4\pi r^2 \frac{1}{m} \frac{\partial}{\partial n^{-1}} \left(\frac{\partial \phi}{\partial \mathbf{r}} \right) \exp[-\beta \phi(\mathbf{r})] \\ &\quad \times \left\langle \sum_{j=1}^N \delta[\mathbf{r} - |\mathbf{x}_{1j}(0)|] \mathbf{x}_{1j}(0) \cdot [\mathbf{x}_1(t) - \mathbf{x}_1(0)] \right\rangle_{(0)} \\ &\quad + O(n)^{-1}, \quad (6) \end{aligned}$$

where the angular bracket with subscript (0) denotes averaging with respect to a system of hard spheres. If we use a Lennard-Jones ($n, \frac{1}{2}n$) potential

$$\phi(\mathbf{r}, n) = \epsilon(\mathbf{r}/a)^{-n} - 2\epsilon(\mathbf{r}/a)^{-n/2} \quad (7)$$

and follow the substitution employed by Rowlinson,