# NOTIZEN

## Some Remarks on the Gaussian Basis Functions

### Application to Methylammonium

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The present work is an attempt to find a way for obtaining both relatively good total molecular energies and calculated molecular geometries, by using a relatively small basis set of Gaussian functions. It was found that if such functions are located in the middle of the bonds too, this goal can be achieved.

The choice of a basis set constitutes a problem when using Gaussian functions in a quantum chemical calculation. The threefold freehand, i. e. the number of functions, their exponents and location make this problem more complicated. For this reason there exist many ways of choosing such a basis set [1–4]. The general method is based on parameter optimization. This is currently being done for the atomic case. When dealing with molecules, it has been suggested that the number of functions be increased instead of making a new optimization, which is a very lengthy process. All these methods are based on energy minimization. The total energy of the system constitutes the criterion for judging the goodness of the chosen basis set.

Some works [5, 6] have dealt with the influence of the chosen basis set on other molecular features than energy. It was found that the best basis set for the total energy is not always the best one for other physical and chemical properties.

In the present work we have tried to find some guide lines of how to choose a basis set in a molecular calculation which yields a relatively good total energy but also a good calculated molecular geometry of the system.

The molecular geometry is generally considered as a derived propertey [7], but there are cases where the geometry of the system plays a certain role in the calculations. For example, it is known that the chemical reactions in the solid state (i. e., the reaction paths) are structure (geometry) dependent [8]. There are cases where the geometry is not known experimentally, and theoretical calculations are used to attempt to determine the geometry as well as the conditions in which the compound can be found experimentally [9]. For such cases, it is important to obtain an accurate calculated molecular geometry. Moreover, the molecular geometry can be determined experimentally with sufficient accuracy so that it can be used also as a criterion for judging the chosen basis set.

### *Calculations and Results*

The calculations were carried out for Methylammonium ion – $(H_3N-CH_3)^+$ – the staggered conformation. A program based on the SCF-MO-LC(LCGO)-method, written by W. Meyer and P. Pulay of this Institute was used. We began with a basis set consisting of 40 "pure" Gaussian functions making 34 groups as shown in Table 1.

Table 1.

| Atom | Type of function | No. of functions | No. of groups |
|---|---|---|---|
| each H | 3 (1s) | 18 | 18 |
| N and C, | 5 (1s) | 10 | 10 |
| respec- | 2 ($p_x$) | 4 | 2 |
| tively | 2 ($p_y$) | 4 | 2 |
| | 2 ($p_z$) | 4 | 2 |
| | | 40 | 34 |

All exponential parameters ($\eta$ values) were taken as the optimized values given by PREUSS [2]. The following geometrical parameters were kept fixed during the calculations:

The HNH and HCH angles ($\alpha$ angles), all equal to 109°.
The HN bond length equal to 1.04 Å and the HC bond length equal to 1.09 Å.

The only geometrical parameter allowed to vary was the C–N interatomic distance ($R$).

Some trial calculations were carried out with a fixed $R$ value and varying the angle $\alpha$ and the hydrogen-heavy atom distances. It was found that the former values for these parameters were the best ones according to the total energy.

The total molecular energy as a function of $R$ showed a minimum at $R=1.63$ Å. This value is too far from

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[1] H. PREUSS, Z. Naturforsch. **11 a**, 823 [1956].
[2] H. PREUSS, Z. Naturforsch. **20 a**, 1290 [1965].
[3] E. CLEMENTI and D. R. DAVIS, J. Comput. Phys. **1**, 223 [1966].
[4] S. HUZINAGA, J. Chem. Phys. **42**, 1293 [1965].
[5] I. G. CSIZMADIA, M. C. HARRISON, J. M. MOSKOWITZ, and B. T. SUTCLIFFE, Theoret. Chim. Acta (Berl.) **6**, 191 [1966].
[6] R. R. HART and M. B. ROBIN, Theoret. Chim. Acta (Berl.) **3**, 375 [1965].
[7] S. F. BOYS and G. B. COOK, Rev. Mod. Phys. **32**, 285 [1960].
[8] G. M. J. SCHMIDT, Reactivity of the Photoexcited Organic Molecule, Interscience 1967.
[9] R. AHLRICHS and W. KUTZELNIGG, Theoret. Chim. Acta (Berl.) **10**, 377 [1968].

the experimental one [10]. We tried to improve our results by increasing the basis set. This was done in two ways:

a) By adding Gaussian functions in the middle of the C–N bond.
b) By taking a larger basis set on each heavy atom.

*Case a)*

Adding one Gaussian with $\eta = 1.562$ a. u. we obtained a lowering of the total energy but no shift in the position of the minimum. However, we observed a trend toward a greater lowering of the energy for smaller values of $R$ (the right direction according to our point of view). By adding a second function at the same location with $\eta = 2.0$ a. u. we obtained, together with a lowering of the energy, a shift of the minimum to $R = 1.58$ Å. A third function with $\eta = 0.5$ a. u. did not change the position of the minimum and the energy decrease was very small. The final results are given in Table 2.

*Case b)*

In this case, we took for the (1s) orbitals on the heavy atoms, 7(1s) functions from the Huzinaga 9(1s) basis set [4]. The p functions and those on the hydrogen were left as in Case a). According to the total molecular energy these functions are better. We obtained a lowering of the energy by about 0.05% compared to Case a). In regard to the geometry the situation was not the same. For this case the minimum is located at $R = 1.62$ Å (Table 2).

*Discussion*

To obtain a shift of the energy minimum to smaller values of $R$ means in fact to be able to increase in some way the attractive term (i. e., to extend the preponderance of the attractive part toward smaller $R$ values) and (or) to decrease the repulsive term. The Gaussian functions we have located in the middle of the C–N bond tend to do this. They increase the nucleus-electron attraction by the fact that these electrons are now shared by the two nuclei. They also decrease the nucleus-nucleus repulsion by constituting a screen.

If all this is true, then functions though located at the middle of the C–N bond but which are more expanded in space (i. e., with small $\eta$ values), have to shift the minimum toward larger values of $R$. In order to check this, we took only two functions in the middle of the bond (the shift in Case a) was observed with the first two functions). Two kinds of calculations were done:

*Case c)*

For this case we took as exponential parameters of the two functions:

$$\eta_1 = 0.3 \text{ a. u.}$$
$$\eta_2 = 0.7 \text{ a. u.}$$

These values correspond to a range of the Gaussians:

$$\varrho_1 = 0.953 \text{ Å}$$
$$\varrho_2 = 0.653 \text{ Å} \qquad \text{where} \quad \eta = 1/\varrho^2.$$

The results, Table 2, indicate a shift of the minimum to $R = 1.64$ Å. The total energy is now lower than in Case a), which means that these $\eta$ values are better according to energy but not to molecular geometry.

*Case d)*

In this case we took more diffuse functions, expanded even beyond the two nuclei. The exponential parameters were:

Table 2.

| $R$ (Å) | Total Energy (a. u.) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Case a) | Case b) | Case c) | Case d) | Case e) | Case f) | Case g) |
| 1.53 | −94.15550 | | | | | | |
| 1.545 | −94.15610 | −94.19792 | | | | | |
| 1.55 | −94.15622 | | −94.15625 | | | | |
| 1.56 | −94.15646 | −94.19933 | | | −94.28261 | | |
| 1.58 | −94.15667 | −94.20067 | −94.15776 | | | −94.29845 | |
| 1.59 | −94.15666 | | | | | | |
| 1.60 | −94.15657 | | −94.15836 | −94.15083 | | | |
| 1.608 | | −94.20157 | | | −94.28800 | −94.29870 | |
| 1.62 | | −94.20164 | | | | −94.29864 | |
| 1.63 | −94.15590 | −94.20155 | −94.15875 | −94.15351 | −94.28953 | −94.29853 | −94.29318 |
| 1.64 | | | −94.15876 | | | | |
| 1.66 | | −94.20061 | −94.15860 | −94.15530 | −94.29070 | −94.29782 | −94.29526 |
| 1.68 | | | | | −94.29099 | | |
| 1.69 | | | | −94.15632 | −94.29099 | −94.29656 | −94.29661 |
| 1.72 | | | | −94.15662 | −94.29049 | | −94.29721 |
| 1.73 | | | | | | | −94.29727 |
| 1.75 | | | | −94.15633 | | | −94.29720 |
| 1.78 | | | | −94.15547 | | | |

[10] L. E. SUTTON, Tables of Interatomic Distances, Spec. Public. 18, The Chemical-Society, London 1965.

$\eta_1 = 0.05$ a. u.
$\eta_2 = 0.10$ a. u. which correspond to:
$\varrho_1 = 1.672$ Å
$\varrho_2 = 2.365$ Å.

The results, Table 2, indicate now a shift of the minimum to $R = 1.72$ Å, as expected. The total energy has also increased.

One can argue that these results are not conclusive enough because we have used a too small basis set and in this case the addition of a new function can result in a large change in energy and geometry. But this is not the case. We have repeated the calculations with the full Huzinaga 9(1s) basis set (Case e). The results, Table 2, indicate an important lowering of the total energy, but the minimum is located now at $R = 1.685$ Å, a value far from the experimental one. In this case, if one tries to add functions at the middle of the C–N bond, as we did, one finds the same screening effect. So, in Case f), putting a function in the middle of the bond with exponential parameter $\eta = 0.7$ a. u., we obtained a lowering of the total energy but also a shift of the minimum to $R = 1.608$ Å, which is an improvement according to geometry (Table 2). If we put now in the middle of the bond a more expanded function (Case g), with exponential parameter $\eta = 0.2$ a. u., the increase in energy is small, of the order of 0.01%, but the minimum is now shifted to $R = 1.73$ Å, as expected (Table 2).

From this, one can conclude that in order to obtain a relatively good calculated geometry, when dealing with Gaussian functions, it is desirable to locate functions in the middle of the bond too, and with such an exponent that they are not too expanded in space.

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## EPR-Untersuchung am Tetracyanochinodimethan-Anion in flüssigen Kristallen

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Die beobachtete Verschiebung der Hfs-Konstanten $\Delta a$ beim Übergang von isotroper zu nematischer Phase läßt sich bekanntlich deuten [1] bei Kenntnis der Ordnungsmatrix $\Theta_{ij}$ und des Hfs-Tensors $A_{ij} = A_{ij}' + a_{\mathrm{iso}}\,\delta_{ij}$:

$$\Delta a = \tfrac{2}{3} \sum_{i,j} \Theta_{ij}\, A_{ij}'. \qquad (1)$$

Für axialsymmetrische Tensoren vereinfacht sich Gl. (1) zu

$$\Delta a = \Theta_{33}\, A_{33}'. \qquad (2)$$

Die Berechnung von $\Delta a$ setzt also neben der Kenntnis des Ordnungsparameters $\Theta_{33}$ die Kenntnis der Hfs-Tensorkomponente $A_{33}'$ im moleküleigenen Koordinatensystem voraus. $A_{33}'$ kann entweder berechnet oder – besser – aus Festkörper-EPR-Spektren gewonnen werden. Die Berechnung von $A_{33}'$ nach MCCONNELL und STRATHDEE [2] unter Verwendung von Slater-Orbitalen führt für $C^{13}$-Kerne in Aromaten mit $Z_{\mathrm{eff}}^{\mathrm{C}} = 3{,}18$ zu recht befriedigenden Ergebnissen [1, 3, 4], jedoch versagt diese Methode beim Tetracyanoäthylen(TCNE)-Anion für $\Delta a$(C) und $\Delta a$(N) [5, 6] und führt zu anomal großen Ordnungsparametern [7] $\Theta_{33} \approx -0{,}5$. Benutzt man dagegen die in glasartig erstarrter Matrix *gemessene* Hfs-Tensorkomponente $A_{33}'$(N) = +3,87 Oe [9], so erhält man in p-Azoxyanisol (PAA) ($\vartheta = 120$ °C) $\Theta_{33} = -0{,}23$, was mit dem aus der $g$-Faktorverschiebung ermittelten Wert [6] verträglich ist. Im flüssigen Kristall Licristal IV (Firma Merck, Darmstadt), der seine nematische Phase im Bereich 16 °C $\leqq \vartheta \leqq$ 76 °C hat, folgt aus dem bei $\vartheta = 17$ °C gemessenen $\Delta a$ und der gemessenen Komponente $A_{33}'$(N) ein $\Theta_{33} = -0{,}31$. Die isotropen Aufspaltungskonstanten sind in beiden Lösungsmitteln gleich.

Von dem Anionradikal des Tetracyanochinodimethans (TCNQ) (Abb. 1) läßt sich $A_{33}'$(N) leider nicht aus dem Glasmatrix-Spektrum bestimmen, da sich das EPR-Spektrum wegen der vergleichbar großen Protonen- und Stickstoff-Hfs-Kopplungen nicht auflösen läßt. Zur Auswertung von $\Delta a$ ist man also auf eine theoretisch gewonnene Tensorkomponente angewiesen. Wir woll-

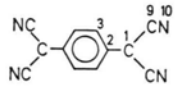


Abb. 1. Tetracyanochinodimethan (TCNQ).

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[5] H. R. FALLE u. G. R. LUCKHURST, Mol. Phys. **11**, 299 [1966].
[6] H. HAUSTEIN, K. MÖBIUS u. K. P. DINSE, Z. Naturforsch. **24 a**, 1764 [1969].
[7] Der von uns in früheren Arbeiten über flüssige Kristalle [4, 6, 8] benutzte Ordnungsparameter $P$ hängt mit $\Theta_{33}$ definitionsgemäß über $P = -2\,\Theta_{33}$ zusammen.
[8] H. HAUSTEIN, K. MÖBIUS u. K. P. DINSE, Z. Naturforsch. **24 a**, 1768 [1969].
[9] J. A. BRIVATI, J. M. GROSS, M. C. R. SYMONS u. D. J. A. TINLING, J. Chem. Soc. **1965**, 6504.

ten untersuchen, ob die nach McConnell und Strathdee berechnete Stickstoff-Tensorkomponente auch beim TCNQ(−) zu einem unvernünftig großen Ordnungsparameter führt und — wenn das der Fall ist — ob sich diese Schwierigkeit umgehen läßt, indem man den am TCNE(−) gemessenen Wert $A_{33}'(\mathrm{N})$ unter Berücksichtigung der leicht unterschiedlichen Spindichten $\varrho^{\mathrm{N}}$ auf das TCNQ(−) überträgt.

TCNQ(−) ließ sich in PAA durch Dissoziation des Lithiumsalzes, auf elektrolytischem Wege (Leitsalz TBAP) und durch Reduktion mit NaJ erzeugen. Die Dissoziation des Lithiumsalzes lieferte eine so günstige Radikalausbeute, daß selbst die Verschiebung der $C_9^{13}$-Satellitenlinien ausgewertet werden konnte. Im folgenden soll deshalb nur über die Messungen an den auf diese Weise erzeugten Radikalionen berichtet werden [10].

Abb. 2 zeigt die Temperaturabhängigkeit der gemessenen Verschiebungen $\Delta a(\mathrm{C_9})$, $\Delta a(\mathrm{N})$ und $\Delta g$. Die für die Ringprotonen gemessene Verschiebung

$$\Delta a(\mathrm{H}) = 13 \pm 7\ \mathrm{mOe}$$

ist betragsmäßig so klein, daß kein Temperaturgang aufgenommen werden konnte. In isotroper Phase wurden folgende Werte gemessen:

$$a(\mathrm{C_9}) = -\,(6{,}966 \pm 0{,}005)\ \mathrm{Oe};$$
$$a(\mathrm{N}) = \phantom{-}\,(0{,}998 \pm 0{,}005)\ \mathrm{Oe};$$
$$a(\mathrm{H}) = -\,(1{,}393 \pm 0{,}005)\ \mathrm{Oe};$$
$$g = 2{,}002693 \pm 2\ \mathrm{ppm}.$$

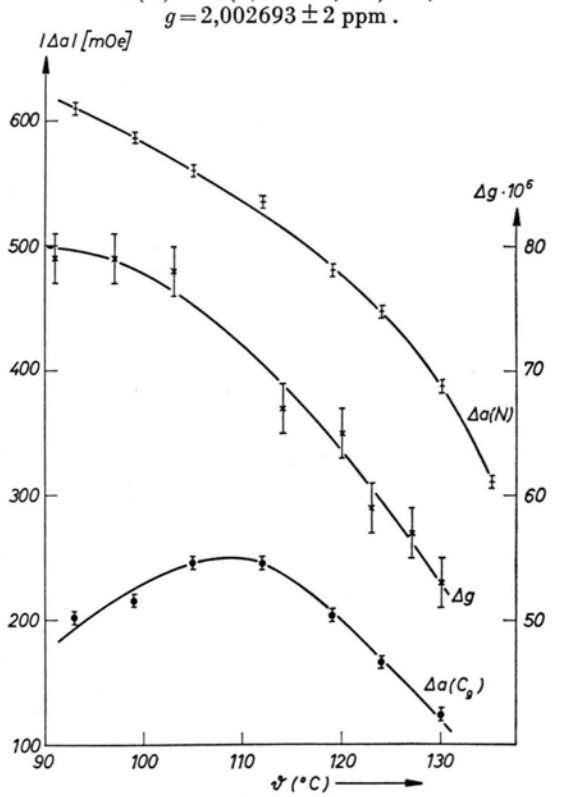


Abb. 2. Temperaturabhängigkeit der Verschiebungen der Hfs-Kopplungskonstanten und des $g$-Faktors vom TCNQ(−) im flüssigen Kristall PAA.

Die Verschiebungen $\Delta g$ und $\Delta a(\mathrm{N})$ spiegeln die erwartete Temperaturabhängigkeit des Ordnungsparameters wider. In Analogie zu Gl. (2) gilt

$$\Theta_{33} = \Delta g_{\mathrm{exp}} / (g_{33} - g_{\mathrm{iso}})\ , \qquad (3)$$

woraus für 120 °C ein Ordnungsparameter $\Theta_{33} = -0{,}21$ folgt. Benutzt man die am TCNE(−) gemessene Hfs-Tensorkomponente $A_{33}'(\mathrm{N})$ und rechnet sie auf die Stickstoff-Spindichte im TCNQ(−) um [$\varrho^{\mathrm{N}}$(TCNE) $= 0{,}076$; $\varrho^{\mathrm{N}}$(TCNQ) $= 0{,}054$ [11]], so folgt nach Gl. (2) für 120 °C: $\Theta_{33} = -0{,}18$. Die gute Übereinstimmung zwischen den nach den beiden Methoden bestimmten Ordnungsparametern rechtfertigt das hier zugrunde gelegte Auswertungsverfahren.

Dagegen führt wieder — wie beim TCNE(−) — die Berechnung von $A_{33}'(\mathrm{N})$ mit Slater-Orbitalen und $Z_{\mathrm{eff}}^{\mathrm{N}} = 3{,}90$ zu dem anomal großen Wert $\Theta_{33} \approx -0{,}5$. Wir berechneten die $C^{13}$-Tensorkomponente $A_{33}'(\mathrm{C_9})$ des als planar angenommenen TCNQ(−) nach [2]

$$A_{33}'(\mathrm{C_9}) = 2\,\{25{,}7\,\varrho_9 - 0{,}40\,\varrho_1 - 0{,}20\,(\varrho_2 + \varrho_{10})\}. \qquad (4)$$

Die nach McLachlan [12] berechnete Spindichte $\varrho_9 = -0{,}0005$ ist sicher mit einem großen relativen Fehler behaftet und führt deshalb auch zu einem entsprechend ungenauen theoretischen Wert $A_{33}'(\mathrm{C_9})$, aus dem man $\Theta_{33}$ nicht bestimmen kann. Man kann aber umgekehrt aus dem gemessenen $\Delta a(\mathrm{C_9})$ und dem aus $\Delta a(\mathrm{N})$ bzw. $\Delta g$ berechneten Ordnungsparameter das Vorzeichen der Spindichte $\varrho_9$ bestimmen: Wegen der absoluten Kleinheit von $\varrho_9$ ist $a_{\mathrm{iso}}(\mathrm{C_9})$ sicher *negativ*. Die beobachtete *positive* Verschiebung $\Delta a(\mathrm{C_9}) \approx 200$ mOe läßt sich wegen der kleinen Fernwechselwirkungsbeiträge in Gl. (4) ($< 60$ mOe) nur für ein $\varrho_9 \approx -0{,}01$ interpretieren.

Die Protonen-Hfs-Konstante verschiebt sich beim Übergang zur nematischen Phase nur sehr wenig ($\approx 10$ mOe). Benutzt man den berechneten [2] Wert $A_{33}'(\mathrm{H}) = -660$ mOe und ein $\Theta_{33} \approx -0{,}2$, so würde man dagegen ein $\Delta a(\mathrm{H}) \approx 130$ mOe erwarten.* Möglicherweise wird diese erwartete Verschiebung durch eine Spindichte-Umverteilung kompensiert, die von einer Einebnung des Moleküls in der nematischen Phase herrührt. Eine Einebnung nichtplanarer Moleküle in der nematischen Phase wurde bereits von anderen Autoren vermutet [1]. Quantitativ brauchte $\varrho_3$ in der isotropen Phase nur um $+0{,}004$ größer zu sein als in der nematischen, um den Verschiebungseffekt $\Delta a(\mathrm{H})$ zu kompensieren. Dieses Abfließen von Spindichte in die Substituenten würde bereits durch ein

[10] Der Einfluß von Leit- und Fremdsalzen auf den Ordnungsparameter wurde eingehend untersucht. Es wurden qualitativ die gleichen Abhängigkeiten festgestellt wie im Falle des TCNE(−) [6].

[11] P. M. Rieger u. G. K. Fraenkel, J. Chem. Phys. **37**, 2795 [1962].

[12] A. D. McLachlan, Mol. Phys. **3**, 233 [1960].

* Wir setzen dabei voraus, daß der Tensor $\Theta_{ij}$ für das TCNE axialsymmetrisch ist. Die Rechnung zeigt, daß sich $a(\mathrm{H})$ nur dann nicht verschiebt, wenn $\Theta_{11} - \Theta_{22} \approx 0{,}6$ gilt. Wir hätten jedoch keine Erklärung für eine so große Anisotropie von $\Theta_{ij}$ in der Molekülebene.

Anwachsen des Resonanzintegrals $\beta_{12}$ in nematischer Phase von 0,90 $\beta_0$ auf 0,95 $\beta_0$ ermöglicht werden.

Das beobachtete Maximum im Temperaturverlauf von $\Delta a(C_9)$ läßt sich qualitativ ebenfalls durch eine Spindichte-Umverteilung verstehen. Wegen der Kleinheit des Effektes und wegen der Komplikation, die durch die Abhängigkeit der isotropen $C_9$[13]-Hfs-Konstante auch von benachbarten Spindichten hervorgerufen wird, schien uns aber eine quantitative Rechnung nicht lohnend.

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## Nuclear Magnetic Relaxation in a Dilute Gas of Spherical Rotors

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In a recent Article [1] in this Journal, McCourt and Hess presented a theoretical treatment of nuclear spin relaxation in a dilute gas of spherical rotors for the case where the relaxation mechanism is governed by the spin-rotation interaction $W_{SR}$. Unlike the earlier analyses [2, 3], the McCourt-Hess calculation focuses on effects associated with the symmetry properties of the molecules and attempts to take these into account. Unfortunately, in deriving a convenient form for $W_{SR}$, serious errors were made in treating these molecular symmetry properties with the result that the arguments upon which the symmetry-related conclusions rest are not valid. It is the purpose of this Note to point out these errors and to discuss briefly some of the associated implications. We select $CH_4$ as a representative spherical rotor and confine most of our detailed remarks to this example.

MH do not attempt to present a complete analysis. They consider only effects associated with "zero-frequency" transitions. These are transitions which conserve both the energy of rigid rotation and the energy of centrifugal distortion [4], so that their frequencies are, in magnitude, $\lesssim |\omega_0|$, where $\omega_0$ is the nuclear larmor frequency. The MH analysis is based on the assumption that only such zerofrequency transitions need be considered, and it is within this framework that the current criticism is presented.

MH specifically exclude effects associated with two types of "high-frequency" transitions. In the first, the rotational quantum number is not conserved and the energy of rigid rotation is changed. In the second, the total nuclear spin quantum number $I$ is not conserved and the energy of centrifugal distortion is changed [5]. The justification for neglecting these transitions [6] lies in the fact that they occur at frequencies whose magnitude is, in general, $\gg |\omega_0|$.

It should be pointed out that there is a third type of highfrequency transition in which $I$ is conserved but the centrifugal distortion energy is not. The possibility of such transitions has not been mentioned previously in the literature. However, because of their high frequency, they are also excluded from the framework of the MH treatment and the present discussion.

Of the many symmetry-related conclusions derived by MH, only one representative result will be quoted here. In Eq. (4.10) of MH, it is shown that, for the limit of extreme narrowing, the spin-lattice relaxation time $T$ is given by

$$\frac{1}{T} = \frac{2}{3}\langle J^2\rangle_0 \left\{ \frac{{c_a}^2}{\omega_{coll}} + \frac{q\,{c_d}^2}{45\,\tilde{\omega}_{coll}} \right\}. \qquad (1)$$

Here $c_a$ is the average spin rotation constant and $c_d$ is the anisotropy in the spin rotation matrix. $\langle J^2\rangle_0$ is the average value of $J(J+1)$. The collision integrals $\omega_{coll}$ and $\tilde{\omega}_{coll}$ are defined, respectively, in Eqs. (3.11) and (3.12) of MH. For tetrahedral molecules, $q=3$; for octahedral molecules, $q=2$ (for values of $J>2$). It is one of the major conclusions of MH that $T$ depends in this manner on the symmetry of the particular spherical rotor under consideration.

Because we are confining our detailed remarks to $CH_4$, we can make direct use of the work of Yi, Ozier and Anderson (Paper I) [4] and of Ozier, Crapo and Lee (Paper II) [7]. These two papers present (among other things) a detailed group theoretical treatment of (1) the spin rotation interaction $W_{SR}$; (2) the necessary spin-rotational wave functions and (3) all the matrix elements required for an analysis which considers only zero-frequency transitions [8].

In Sec. III.A of Paper I, there is defined a representation $\Gamma$ which takes into account all the symmetry requirements which the wave functions must satisfy. Al-

[1] F. R. McCourt and S. Hess, Z. Naturforsch. **25 a**, 1169 [1970].
[2] M. Bloom, F. Bridges, and W. N. Hardy, Can. J. Phys. **45**, 3533 [1967].
[3] J. S. Blicharski, Physica **39**, 161 [1968].
[4] P. N. Yi, I. Ozier, and C. H. Anderson, Phys. Rev. **165**, 92 [1968]. This work is referred to as Paper I.
[5] The fact that a change in I implies a change in the centrifugal distortion energy is discussed in Sect. III.A of Paper I. Notice that this fact is true only for the tetrahedral molecule $XY_4$ if the spin of nucleus Y is 1/2. It is not true for other tetrahedral molecules or any octahedral molecules.
[6] It is understood that one is also neglecting transitions in which both $I$ and $J$ change.
[7] I. Ozier, L. M. Crapo, and S. S. Lee, Phys. Rev. **172**, 63 [1968]. This work is referred to as Paper II.
[8] Note that $e_i\,e_i$ $(i=1, 2, 3, 4)$ in MH is $-\frac{1}{3}\,\varepsilon^i$ in Refs. [4, 7].

though MH do not explicitly introduce any representation, their arguments implicitly assume one, and it is clear that this assumed representation is *not* equivalent to $\Gamma$. This selection of an inappropriate representation is the fundamental error in the MH treatment and leads to three errors in the detailed development of the effective spin rotation operator given in Eq. (2.13) of MH. We shall consider each of these in turn.

(1) The total nuclear spin $I$ is a good quantum number [9] in a dilute gas and can equal 2, 1 or 0. The constant $c_d$ contributes *only* to the relaxation of the $(I=1)$ species and *not* to the relaxation of the $(I=2)$ species [4]. No account of this fact is taken in MH.

(2) While the MH treatment clearly fails for the $(I=2)$ species, it may still be valid for the $(I=1)$ case. However, for this case, it can be shown that the simplification of Eq. (2.9) of MH is not correct. This equation can be written

$$I' = L_1 + L_2 \tag{2}$$

where
$$L_1 = -\tfrac{1}{2}\,[I^{(1)} + I^{(2)} + I^{(3)}] \cdot \overline{e_4\, e_4} \tag{3}$$

and
$$L_2 = -\tfrac{1}{2}\,[I^{(1)} \cdot \overline{e_2\, e_2} + I^{(2)} \cdot \overline{e_1\, e_1} + I^{(3)} \cdot \overline{e_3\, e_3}]\,. \tag{4}$$

If we use the notation of Papers I and II, then

$$L_1 = L_A + L_B \tag{5 a}$$

and
$$L_2 = L_A - L_B\,, \tag{5 b}$$

where
$$L_A = -\tfrac{1}{6} \sum_{\xi=xyz} I^\xi \cdot \varepsilon^\xi \tag{6 a}$$

and
$$L_B = -\tfrac{1}{6}[I^x \cdot (\varepsilon^y + \varepsilon^z) + I^y \cdot (\varepsilon^z + \varepsilon^x) + I^z \cdot (\varepsilon^x + \varepsilon^y)]\,. \tag{6 b}$$

It can be shown [7] by simple group theory (or by direct evaluation) that, in representation $\Gamma$, $L_B \cdot J$ has no non-zero matrix elements diagonal in $I$. Since transitions off-diagonal in $I$ are being neglected, we can, within the context of the present problem, write

$$L_1 = L_2\,. \tag{7}$$

Yet in MH, $L_2$ is set equal to zero and only $L_1$ is retained.

(3) The MH calculation can be modified so as to take Eq. (7) into account simply by multiplying $c_d$ by a factor of two. However, the analysis leading from Eq. (2.12) to Eq. (2.13) of MH is also incorrect. The operator

$$H_{SR} \equiv \overline{e_4\, e_4} \cdot J \tag{8}$$

plays the role of a spin-rotational magnetic field. MH argue that $\tilde{I} \cdot H_{SR}$ has non-zero matrix elements diagonal in $J$ only for the component of $H_{SR}$ along $J$. They then apply arguments equivalent to the use of a simple vector model to obtain

$$H_{SR} = \alpha J\,, \tag{9}$$

where

$$\alpha = \left(\frac{K^2}{J(J+1)} - \frac{1}{3}\right). \tag{10}$$

Here $K$ is the quantum number associated with the projection of $J$ on the "4" axis defined MH.

However, when the matrix elements of $\tilde{I} \cdot \alpha J$ are evaluated in representation $\Gamma$, it is found that they all vanish. This results is not surprising since $\tilde{I} \cdot \alpha J$ has only non-zero matrix elements diagonal in $K$, whereas the complete expression for the tensor part of the spin rotation interaction has only non-zero matrix elements off-diagonal in $K$, as can be seen from Eq. (A4) of Paper II [10]. An assumption equivalent to Eq. (9) was made by GORDON [11] in analysing the magnetic-resonance molecular-beam spectrum of $CH_4$ observed by ANDERSON and RAMSEY [12] and was, in part, responsible for the fact that the Gordon analysis gave incorrect results [7].

It is clear from arguments (1), (2) and (3) presented here that the expressions [e. g. Eq. (1) above] for the spin-lattice relaxation times derived in MH for tetrahedral molecules are not correct. Although we have not discussed the octahedral case here, it is felt that a reexamination of this part of the problem is in order as well.

In Sec. 5 of MH, the data available in the literature on $c_d$ for $CH_4$ is reviewed in the light of the MH treatment and it is concluded that the best value for $|c_d|$ is 21.0 kHz [12, 7], rather than 18.2 kHz [13]. It is clear from our remarks here that the basis for this conclusion is not valid. In fact, the best current value for $c_d$ is $+(18.5 \pm 0.5)$ kHz, as obtained by YI, OZIER, and RAMSEY [14].

In spite of the difficulties in the MH treatment, this work represents a significant step forward. Besides pointing out the possibility that symmetry considerations may be important, they extend the kinetic equation approach to the problem of NMR in polyatomic molecules and show many of the advantages of this technique over the correlation function approach. When the treatment of $W_{SR}$ has been modified so as to include the symmetry requirements correctly, the MH calculation will be very helpful in the analysis of spin-lattice relaxation data on spherical rotors.

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[9] It should be kept in mind that we are referring here specifically to $CH_4$.

[10] While MH originally referred $K$ to the "4" axis, MH subsequently showed that $K$ (as defined in MH) could equally well be referred to any arbitrary axis fixed in the molecule. Thus, for example, $K$ can be associated with the $Z$ axis of the molecule-fixed frame shown in Fig. 1 of Paper I. This particular choice is the most convenient one for comparing MH to Papers I and II.

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