Multiple Pulse Proton Magnetic Resonance Study of KHCO₃ and KHSO₄

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Single crystals of KHCO₃ and KHSO₄ have been investigated by solid state high resolution proton magnetic resonance techniques. These compounds may be considered as model systems for compounds that contain abundant quadrupolar nuclei (³⁹K) with small magnetogyric ratio in addition to the protons. Despite considerable line broadening resulting from ¹H-³⁹K dipeptide-dipole coupling, all four possible proton shielding tensors in KHSO₄, and an averaged shielding tensor for the two different proton sites in KHCO₃ could be measured accurately. The results are analysed to determine the degree of ionization of the protons in the three types of hydrogen bonds occurring in KHCO₃ and KHSO₄.

1. Introduction

Multiple pulse techniques for high resolution NMR in solids have now been applied successfully for measuring proton shielding tensors in a variety of solids.¹ ². The simplest contained no other nuclear species with magnetic moments in addition to the protons so suppression of the ¹H—¹H dipole-dipole interactions with any of the standard multiple pulse sequences ³ did lead to “high-resolution” spectra. Others contained, in addition to the protons, further abundant spin-1/2-nuclei, e.g., ¹⁹F or ³¹P. Simultaneous homo-hetero-decoupling has been demonstrated to work in these cases ³—⁵. On the other hand, it does not seem feasible in general to decouple quadrupolar nuclei from protons in solids. Exceptions are ¹H and possibly a few other nuclei with small nuclear quadrupole moment eQ. For some nuclei with very large eQ, or more precisely, with very large quadrupole coupling constants e²Q, heterodecoupling may not be needed for achieving “high resolution” in the proton spectrum because of the phenomenon of “selfdecoupling”.⁶ Here we describe the investigation of single crystals of KHCO₃ and KHSO₄ where the protons are dipole coupled to the abundant quadrupolar ³⁹K-nuclei. KHCO₃ and KHSO₄ may be considered to be typical representatives of the class of compounds that contain abundant I > 1/2 nuclei with small magnetic moments — the magnetic moment of ³⁹K is only 0.4 nuclear magnetons — and for which no effective selfdecoupling may be expected. Our results show that accurate measurements of proton shielding tensors can be accomplished in such compounds even in the presence of heteronuclear dipolar line broadening.

All the protons in KHCO₃ and KHSO₄ are involved in hydrogen bonds. In KHSO₄ there are two different types of hydrogen bonds (see below). Any study of a hydrogen bond by its shielding tensor beyond just establishing numbers requires either an empirical or a theoretical basis. Gierke and Flygare ⁸ have put forth a simple theory for shielding tensors whose application to protons forming hydrogen bonds has revealed, among other things, the physical origin of the dominant contributor to the proton shielding anisotropy: it is the Larmor-precession induced by the applied field B₀ of the electrons of the hydrogen bonded atoms ¹. This has been confirmed recently by much more sophisticated ab-initio calculations of some model hydrogen bonds carried out by Ditchfield et al. ⁹ This adds to our confidence to use the GF-theory for extracting information from our shielding data on the degree of ionization of the hydrogens in the three types of hydrogen bonds studied in this work.

2. Crystal Structures, Number of NMR Lines Expected from Crystal Symmetry

(a) KHCO₃

Crystals of KHCO₃ are monoclinic, space group P₂₁/c, a = 15.17 Å, b = 5.63 Å, c = 3.17 Å, β = 104.6°, with Z = 4 molecules in the unit cell. The...
HCO$_3^-$-anions form dimers, linked by two adjacent hydrogen bonds. The two protons of each dimer are related by a center of symmetry (see Fig. 1) and are, therefore, magnetically equivalent. As there are two orientationally inequivalent dimers, the solid state high resolution spectrum is expected to consist of two lines in general. The two types of dimers are related by the monoclinic glide plane (the $a^*$-$c$-plane) so all protons in KHCO$_3$ have the same set of principal shielding components and one line only is expected in the proton spectrum for the special case when $B_0$ lies in the glide plane. As regards the principal shielding directions we expected from the results of previous solid state PMR studies of hydrogen bonds (for a review see Ref.$^1$) that the most shielded directions would be approximately parallel to the directions of the hydrogen bonds and that the least shielded directions would be close to the normals of the quasi-planes formed by the dimers. As Fig. 1 shows, all these directions lie for both types of dimers not far from the monoclinic glide plane. A rotation of the crystal about the $b$-axis, i.e. for $B_0$ moving in the $a^*$-$c$ plane, should therefore directly reveal approximate values for two of the three principal shielding components. On the other hand, a rotation about the $c$-axis is most suited to detect, by a splitting of the proton resonance, the expected difference of the orientations of the most shielded proton directions for the two types of dimers. For these reasons we choose the $b$ and $c$ axes as rotation axes for two of our samples. In order to have an orthogonal set of three axes we choose $a^*$ as the rotation axis for a third sample. These samples will be referred to as $a^*$, $b$ and $c$ crystals.

(b) KHSO$_4$

Crystals of KHSO$_4$ are orthorhombic, space group $Pbca$, $a = 8.40$ Å, $b = 9.79$ Å, $c = 18.93$ Å; $Z = 16$.$^{11}$ The system of hydrogen bonds is particularly interesting in KHSO$_4$: the crystal may be considered as consisting of two independent but mutually interpenetrating sublattices, one of which is formed by (HSO$_4^-$)$_2$ dimers held together by two adjacent hydrogen bonds similar as in KHCO$_3$, whereas the other consists of infinite chains, also linked by hydrogen bonds (see Figure 2). Of both the dimers and the chains there are two orientationally (magnetically) inequivalent species, but the protons of all the dimers and of all the chains, respectively, are crystallographically equivalent, so we expect four different proton shielding tensors in KHSO$_4$, but only two different sets of principal components.

As all the hydrogen bonds are lying approximately in the $a$-$b$-plane, it is but natural to use the $a$, $b$, and $c$ axes as rotation axes for the NMR work. For analogous reasons as outlined above for KHCO$_3$ rotation of the KHSO$_4$ crystal about the $c$-axis ($B_0$ moving in the $a$-$b$-plane) should and does give the most valuable information.
3. Experimental

3.1. Preparation of Samples

KHCO₃: Three samples were cut from one large single crystal of KHCO₃ obtained from Prof. Hausühl, University of Cologne. They were preoriented using an optical goniometer, shaped into cylinders (4 mm diameter, 6 mm length), precisely oriented by means of X-ray precession photographs and glued to glass rods carrying discs with angular scales such that their a*, b, and c-axes, respectively, were parallel to the rod axes. The relatively large linewidths in the “high resolution” solid state proton spectra did not warrant the effort to shape spheres for eliminating bulk susceptibility effects.  

KHSO₄: A single crystal cube (length of edge = 4 mm) of KHSO₄ was purchased from Minhorst, Kristallchemie GmbH, D-5431 Meudt, FRG. It was cut such that its edges were parallel to the crystallographic a, b, and c-axes. It was glued with one of its faces to the end of a glass rod as were the KHCO₃ crystals. After completing the NMR data acquisition for this rotation axis, it was removed and reglued with a different face. The procedure was then repeated for the third axis. The orientation was checked each time as described for KHCO₃.

3.2. NMR

In order to achieve “high resolution” in the solid state proton magnetic resonance spectra, we applied the flip-angle error and phase-error compensating version of the MREV-eight-pulse sequence. This sequence consists of π/2-rf pulses with quadrature phases, applied at t and 2t intervals. The width of the π/2-pulses was about 75 μsec, t was chosen as 4 μsec and the operating frequency of the spectrometer was 90 MHz. We point out that whereas homonuclear DD interactions are suppressed very efficiently with the MREV sequence, heteronuclear DD interactions are scaled down only by a factor of roughly 1/2. Multiple pulse single shot 1k-FT spectra were taken at 10° steps of azimuthal angle for each of the rotation axes a*, b, and c for KHCO₃, and at 5° steps for the rotation axes a, b, and c for KHSO₄. TMS was used as an external reference, its signal recorded for each set of measurements and the “scaling factor” checked occasionally.

We measured T₁ of a powder sample of KHCO₃ at room temperature and obtained T₁ = 5.8 minutes, accordingly data for multiple pulse FT spectra were acquired every 5 minutes. Judging from the signal heights at different orientations of the crystals, the orientational dependence of T₁ appears to be small.

The proton T₁ in KHSO₄ is much longer, so data could be acquired only every 1 1/2 hours.

4. Results and Discussion

KHCO₃

Figure 3 shows three characteristic multiple pulse FT spectra of KHCO₃, the upper two are from the b-crystal at azimuthal angles such that the single line possible is at its extreme up- and down-field position; the bottom one is from the c-crystal in the orientation most favourable for a separation of the two possible lines. But neither in this nor in any other spectrum recorded is there any indication of a splitting of the two lines corresponding to the two types of dimers in KHCO₃. Therefore, our data of the line positions allow us to determine only a single shielding tensor which is the average shielding tensor for the two types of protons (dimers) in KHCO₃. Two of the principal axes of the shielding tensor must lie in the a*-c glide plane by crystal symmetry (see Figure 1). In this connection it is worth remarking that a deuteron study of
KDCO$_3$\textsuperscript{14} also failed to distinguish two magnetically inequivalent deuterons, although quadrupolar deuteron line splittings are much larger than chemical shifts of protons. The orientational dependence of the PMR line position is shown in Figure 4.

![Fig. 4. Orientational dependence of PMR line position for KDCO$_3$.](image)

The curves are the results of a least squares computer fit. In all three rotation patterns the least shielded values are roughly the same, this means that $\vec{\sigma}$ must be approximately axially symmetric\textsuperscript{1}. Moreover, the line position varies very slightly only for $B_0$ rotating in the $b$-$c$-plane, the unique axis of $\vec{\sigma}$ must therefore be close to $a^*$ and the principal values of $\vec{\sigma}$ can be read off immediately from the patterns with $b$ as rotation axis. The orientation of $\vec{\sigma}$ is in good agreement with our expectations discussed in section 2: the maximum shielding is observed in "pattern $b$" at $\varphi = 25^\circ$, this is just the orientation of the projections on the $a^*$-$c$ glide plane of both of the hydrogen bond directions. The least shielded direction (at $\varphi = 115^\circ$) corresponds to the normals of the dimers. These semi-quantitative results were refined by a least squares simultaneous computer fit of all of our spectral data of KHCO$_3$. The results relative to TMS are:

$$\begin{align*}
\sigma_{XX} &= -26.8 (\pm 1) \text{ ppm }, \\
\sigma_{YY} &= -23.2 (\pm 1) \text{ ppm }, \\
\sigma_{ZZ} &= +1.7 (\pm 1) \text{ ppm }.
\end{align*}$$

Two of the Euler angles ($\Phi$ and $\psi$: Goldstein convention\textsuperscript{15}) specifying the orientation of the principal axes system of $\vec{\sigma}$ relative to the $a^*$, $b$, $c$-frame are fixed by crystal symmetry to $90^\circ$, the third is found to be $\Theta = 68^\circ (\pm 2^\circ)$.

The reason why we failed to distinguish, as we had wished, the two magnetically inequivalent protons in KHCO$_3$ by two resolved NMR lines is twofold: (i) the individual lines are strongly broadened by mechanisms to be discussed presently. (ii) as a result of the coplanarity of the dimers and of the smallness of the angle $\alpha = 4.7^\circ$ between the $a^*$-$c$-plane and the two different hydrogen bond directions, the orientations of the shielding tensors $\sigma_1$ and $\sigma_2$ of proton types 1 and 2 do not differ much which means that the shift of the two possible PMR lines with respect to each other remains small for all orientations of $B_0$.

In order to assess how much of the observed linewidth $\delta v_{\text{exp}}$, and of its orientation dependence (Fig. 5, upper curve), can be traced back to un-

![Fig. 5. Orientational dependence of PMR line width for KHCO$_3$. Upper curves: experimental; lower curves: theoretical contribution to linewidth from $^{39}$K-$^1$H DD interactions.](image)

resolved line splitting, we have to estimate the contributions of (at least) three line broadening mechanisms: (i) instrumental effects, (ii) residual $^1$H-$^1$H dipolar line broadening and (iii) line broadening by unaveraged heteronuclear $^1$H-$^{39}$K DD interactions.

From the width of lines in $^1$H multiple pulse FT spectra of compounds without heteronuclei, the combined contribution to $\delta v_{\text{exp}}$ of (i) and (ii) can be estimated to be of the order of 120 Hz, and little angular variation is expected. In an attempt to get an estimate for (iii) we calculated the scaled contribution of the $^{39}$K-ions to the second moment of the PMR line by the Van-Vleck formula\textsuperscript{16}. We are well aware that the applicability of this formula to our case is somewhat doubtful because of the modifications of the $^{39}$K-Zeeman levels by the $^{39}$K quadrupole-electric field gradient interaction\textsuperscript{7}. The strength of the latter is not known for KHCO$_3$, but it may be assumed to be fairly small\textsuperscript{17} because...
KHCO₃ is an ionic crystal. Therefore, we may reasonably hope that the Van-Vleck-formula yields at least qualitatively correct values for the linewidths. The results of this calculation are shown by the lower curves in Figure 5. The comparison with the experimental results shows that $\delta r_{\text{exp}}$ and in particular its orientational dependence are mainly due to $^1\text{H}-^{39}\text{K}$ DD interactions. Most of the remaining difference is well accounted for by mechanisms (i) and (ii) and there is little left that can be ascribed to unresolved line splitting. This conclusion is supported by the observation that there is no systematic difference of $\delta r_{\text{exp}} - \delta r_{\text{calc}}$ for rotation pattern b, where unresolved line splitting is absent by crystal symmetry, and rotation patterns $a^*$ and c, where a line splitting is possible in principle. This all is to the point that the angle $\beta$ between the $a^*\cdot c$ plane and the unique axes of $g_1$ and $g_2$ must be small. In fact $\beta = a \left( = \pm 4.7^\circ \right)$ is entirely consistent with our data and $9^\circ$ is a conservative estimate for the upper limit of $|\beta|$.

**KHCO₃**

Figure 6 shows a typical multiple pulse FT spectrum of KHCO₃ with $B_0$ lying in the $a\cdot b$-plane. Two spectral features are clearly resolved, but from symmetry considerations (Sect. 2) we expected four PMR lines. In contrast to the case of KHCO₃, however, both resolved features show clear evidence for being composite lines. From such spectra the line positions and intensities can be determined with sufficient accuracy so that the rotation pattern for $B_0$ moving in the $a\cdot b$-plane can be analysed in terms of four different lines corresponding to the four magnetically different protons in KHSO₄. For $B_0$ moving in the $a\cdot c$ and $b\cdot c$ planes, at most two such distinct lines could be discerned. The data shown in Figs. 7 could be analysed by the least squares fit program mentioned above to yield the four shielding tensors $g^{(a)} \ldots g^{(d)}$ shown in Table 1.

![Fig. 7. Orientational dependence of PMR line positions for KHSO₄.](image)

**Table 1. Proton shielding tensors in KHSO₄.** The principal components are given relative to liquid TMS. $\Phi$, $\Theta$, $\Psi$ are the Euler angles (Goldstein convention [15]) specifying the orientation of the shielding principal axes system to the crystallographic $a$, $b$ and $c$-axes. See text for an assignment of sites a – d to particular protons.

<table>
<thead>
<tr>
<th>site</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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<tr>
<td>$\sigma_{XX}$ [ppm]</td>
<td>-21.6</td>
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<td>-24.3</td>
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<td>$\sigma_{YY}$ [ppm]</td>
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</tr>
<tr>
<td>$\sigma_{ZZ}$ [ppm]</td>
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<tr>
<td>$\Theta$</td>
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<td>+89.3°</td>
<td>+91.6°</td>
<td>+91.8°</td>
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<td>$\Psi$</td>
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<td>+7.5°</td>
<td>+12.3°</td>
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As discussed in Sect. 2 we expected — and obtained indeed — four distinct shielding tensors, but only two different sets of principal components. This is borne out by our results: \( \sigma_{ax}^{(a)} \approx \sigma_{ax}^{(b)} \) and \( \sigma_{ax}^{(c)} \approx \sigma_{ax}^{(d)} \) for \( \alpha = X, Y, Z \). From this finding we conclude (i) \( (\varrho^{(a)}, \varrho^{(b)}) \) and \( (\varrho^{(c)}, \varrho^{(d)}) \) belong to crystallographically equivalent protons, respectively, and (ii) the differences \( \delta_{ax}^{(a)} - \delta_{ax}^{(b)} \) and \( \delta_{ax}^{(c)} - \delta_{ax}^{(d)} \) are a good measure for the experimental accuracy. The root of the mean square of these differences is 0.37 ppm.

On the basis of the data shown in Fig. 7, there is, unfortunately, no way of telling which of the pairs of shielding tensors should be assigned to the protons of the dimers and which to the protons of the chains. On the basis of the experience\(^1\) that the most shielded direction for a proton in a hydrogen bond coincides closely with the direction of the bond itself, we propose, however, that \( \varrho^{(a)} \) and \( \varrho^{(b)} \) belong to the dimers while \( \varrho^{(c)} \) and \( \varrho^{(d)} \) belong to the chains. In order to see that this assignment indeed gives the best agreement with the postulated parallelism of bond and most shielded direction, we first note that all the hydrogen bond directions as well as all the \( Z \)-axes of \( \varrho^{(a)} \) through \( \varrho^{(d)} \) fall closely into the \( a-b \)-plane (\( \Theta^{(a)} \approx \ldots \approx \Theta^{(d)} \approx 90^\circ \)).

The close parallelism of the oxygen-oxygen line and its introduces about 3 — 8 ppm. At first sight it may look disturbing that the ten- sors of shielding of hydrogen bonds consistently overestimate the shielding anisotropy \( \lambda_0 \). Its intro- duction may be justified on the grounds that the GF approach inherently assumes that the proton is well outside of the electronic charge distributions of neighbouring atoms or ions, an assumption which certainly is not fulfilled very well by the bonded oxygen atoms of a hydrogen bond. For this reason we apply \( \varrho^{(d)} \) (bonded oxygen atoms) to the dimers, which, however, dominates \( \lambda_0 \). The other parameter, \( \varepsilon \), is a measure for the ionic character of the hydrogen bond. \( \varepsilon = 0 \) means the hydrogen is fully ionized, \( \varepsilon = 1 \) means the hydrogen carries one full electronic charge in a free-atom-1s-orbital. Term I of the GF-expansion of \( \varrho^{(d)} \), i.e. \( \varrho_{iso} \) (free atom), is to be multiplied by \( \varepsilon \). Neglecting as usual term III
of the GF-expansion, the equations for $\Delta \sigma$ and $\sigma_{||}$ read as follows:

$$\Delta \sigma_{\text{cal}} = R \cdot \Delta \sigma^{\text{IV}}_{\text{b.o.}} + \Delta \sigma^{\text{IV}}_{\text{o.a.}} + R \cdot \Delta \sigma^{\text{IV}}_{\exp}, \quad (1)$$

$$\sigma_{|| \text{cal}} = R \cdot \sigma^{\text{IV}}_{\text{b.o.}} + \sigma^{\text{IV}}_{\text{o.a.}} + \varepsilon \cdot \sigma_{\exp}^{(0)} \cdot (\text{H-atom}) \Delta \sigma_{|| \text{exp}} \quad (2)$$

with $\sigma^{\text{IV}}_{\text{b.o.}} = \sigma^{\text{IV}}$ (bonded O-atoms) and $\sigma^{\text{IV}}_{\text{o.a.}} = \sigma^{\text{IV}}$ (other atoms).

The exclamation signs mean that $R$ and $\varepsilon$ should be adjusted to satisfy these equations. $\sigma_{\exp}^{(0)}$ (H-atom) $= +17.8$ ppm. Evaluation of $\sigma^{\text{IV}}_{\text{b.o.}}$ requires knowledge of the mean squared distance $\langle \varrho^2 \rangle$ of the oxygen's electrons from the oxygen nucleus $\ast$. In previous work on ionic systems $\ddagger$ we have taken weighted averages of $\langle \varrho^2 \rangle$ derived from Malli and Fraga's theoretical data $\dagger$ for the susceptibilities of O and O$^\text{+}$. Comparing these data, which by the nature of the calculation are "free space" susceptibilities, with susceptibilities $\chi$ actually measured in solids $\ddagger$, we come now to the conclusion that Malli and Fraga's value for $\varrho^2_0$, which is equivalent to $\langle \varrho^2 \rangle_0 \approx 1.7 \times \langle \varrho^2 \rangle_0$ is inappropriate for solids and that the value for the neutral oxygen, $\langle \varrho^2 \rangle_0 = 3 \times 10^{-16}$ cm$^2$ is the best choice also for partly ionic systems such as KHCO$_3$ and KHSO$_4$. For the internuclear distances, also required for the evaluation of $\varrho^2_0$, we relied on the X-ray data.10,11

As regards $\varrho^2_0$, the so-called spin-rotation term $\ddagger$ we know that its "parallel" component vanishes to the extent we can localize the origin of this term to the linear entity O...H...O$^\text{22}$. $\varrho^2_0$, therefore, does not show up in Eq. (2) and $\Delta \varrho^2 = -\sigma_{||}$. For $\varrho^2_0$ we use a former guess $\ddagger$ of +16 ppm, the sign of which

is typical for linear structures $\ddagger$ and the size of which is at least consistent with the measured spin-rotation-tensor for the H$_2$O molecule $\dagger$. Table 2 summarizes the results of the calculations.

Table 2. Parameters used to determine, and results for $R$ and $\varepsilon$.

<table>
<thead>
<tr>
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<th>KHCO$_3$</th>
<th>KHSO$_4$ dimers</th>
<th>KHSO$_4$ chains</th>
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<tbody>
<tr>
<td>$\Delta \sigma_{\exp}$ [ppm]</td>
<td>27</td>
<td>24.2</td>
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<tr>
<td>$\sigma_{</td>
<td></td>
<td>\exp}$ [ppm]</td>
<td>33</td>
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<tr>
<td>$\Delta \sigma^{\text{IV}}_{\text{b.o.}}$</td>
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<td>0.7</td>
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<tr>
<td>$R$</td>
<td>0.79</td>
<td>0.85</td>
<td>0.76</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.24</td>
<td>0.42</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The main conclusion we draw is that in all three hydrogen bonds a large part of the hydrogen's charge has been drawn off by the bonded oxygen atoms ($\varepsilon = 0.24$, 0.42 and 0.32 for the dimers in KHCO$_3$ and KHLO$_4$, and for the chains in KHSO$_4$, respectively). This conclusion is not substantially altered even if our guess for $\sigma_{\text{b.o.}}^\text{IV}$ is in error by as much as $\pm 6$ ppm. We also note that our numbers for $\varepsilon$ compare favourably with the results of "population analyses" carried out by Ditchfield et al. for some model hydrogen bonds $\ddagger$. Reversing the flow of arguments, this can also be taken as a support of the simple GF approach, including the introduction of the empirical reduction factor $R$ to be applied to $\sigma^{\text{IV}}_{\text{b.o.}}$, and of our guess of $\sigma_{\text{o.a.}}^\text{IV}$.

Acknowledgements

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$\ast$ Taking GF's definitions and notation, actually not $\langle \varrho^2 \rangle_n$ but $1/Z_n \langle \varrho^2 \rangle_n$ is the mean squared distance of the electrons from nucleus $n$, with $Z_n$ = atomic number of nucleus $n$.


$\ddagger$ H. Goldstein, Classical Mechanics, Addison-Wesley, Reading 1959.
21 W. R. Myers, Rev. Mod. Phys. 24, 15 [1952].