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An Interpretation of the Nuclear Quadrupole Coupling Constant for the HCl Molecule on the Basis of an “Ab Initio” Calculation

By

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The results of a LCAO MO SCF calculation of the quadrupole coupling constant of chlorine in the HCl molecule (carried out with a fairly extended set of basic orbitals) are analyzed. Sensible deformations of the internal shells and of the p_σ -bonding, p_σ -lone pair and p_π type orbitals of the valence shell of chlorine are evidenced.

Die Ergebnisse einer verhältnismäßig ausgedehnten LCAO-MO-SCF-Rechnung zur Bestimmung der Quadrupolkopplungskonstanten für Chlor in HCl werden untersucht. Die Verzerrungen, die der Rumpf und die verschiedenen Zustände der Valenzschale erleiden, werden dabei gesondert wiedergegeben.

Les résultats d'un calcul LCAO-MO-SCF (avec un jeu d'orbitales assez étendu) de la constante de couplage quadripolaire du Cl dans la molécule de HCl sont analysés. On trouve que et les couches internes et les orbitales p_σ liante, p_σ libre et p_π de la couche de valence du chlore sont sensiblement déformées.

The “a priori” evaluation of a variable associated with a one-electron operator, such as the quadrupole coupling constant e^2qQ_A in an isolated molecule, requires, beside the knowledge of the nuclear quadrupole moment eQ_A of the nucleus A , also a very accurate calculation of the ground state wave function of the molecule, which is necessary to evaluate the electric field gradient eq .

When the electronic wave function is represented by a single Slater's determinant, in the SCF-LCAO-MO approximation, the expectation value of the field gradient, can be written as:

$$eq = 2 \operatorname{tr} \mathbf{R}(eq) - e \sum_{\alpha} Z_{\alpha} (3 \cos^2 \vartheta_{A\alpha} - 1) / r_{A\alpha}^3, \quad (1)$$

where $\mathbf{R} = \mathbf{C} \mathbf{C}^\dagger$, and \mathbf{C} is the rectangular matrix of the coefficients which describe the molecular orbitals as linear combinations of a set of pre-selected basic functions χ ; eq is a matrix with elements:

$$(eq)_{rs} = e \int \chi_r^*(1) [(3 \cos^2 \vartheta_{1A} - 1) / r_{1A}^3] \chi_s(1) d\tau;$$

r_A and $\vartheta_{A\alpha}$ (measured with respect to the z axis), define the position of the generic nucleus α , having a charge Z_α , with respect to the quadrupolar nucleus A .

The lack of sufficiently approximate wave functions has led to the assumption of simplifying hypotheses. Therefore, it will be useful to reinterpret the results of a completely “ab initio” calculation using chemical intuition to make evident, as much as possible, the various contributions to the field gradient. To this purpose, the results of a SCF-LCAO-MO calculation will be used, that have been carried

out by the Authors [7] by the direct minimization of the energy through the density matrix \mathbf{R} , as first proposed by McWEENY [4].

The selected set of basic functions is sufficiently more extended than the necessary minimum and is composed of 19 Slater-type functions, of which the orbital exponents are reported in Tab. 1. It is to note that this set cannot describe

Table 1. *Basis functions used for HCl*

	orbital exponent		orbital exponent
$1s_H = \hbar$	1.27	$2p_{zCl} = 2x$	8.35
$2p_{\sigma H} = p$	2.20	$2p_{zCl} = 2\xi$	4.50
$1s_{Cl} = 1s$	16.7	$3p_{zCl} = 3x$	2.64
$2s_{Cl} = 2s$	8.35	$3p'_{zCl} = 3\xi$	1.42
$2s'_{Cl} = 2\sigma$	4.50	$2p_{yCl} = 2y$	8.35
$3s_{Cl} = 3s$	2.64	$2p'_{yCl} = 2\eta$	4.50
$3s'_{Cl} = 3\sigma$	1.42	$3p_{yCl} = 3y$	2.64
$2p_{zCl} = 2z$	8.35	$3p'_{yCl} = 3\eta$	1.42
$2p'_{zCl} = 2\zeta$	4.50		
$3p_{zCl} = 3z$	2.64		
$3p'_{zCl} = 3\zeta$	1.42		

the small percent of π bonding that the molecule very probably has [5], and that the energy has not been minimized with respect to the orbital exponents.

In Tab. 4 of ref. [7] the matrices \mathbf{R} and (eq) , which are necessary for calculating equation (1), are reported. It is found:

$$eq = (eq)_{el} + (eq)_{nucl} = 2 \operatorname{tr} \mathbf{R}(eq) - 2 \frac{e}{r_{HCl}^3} = 3.789 + 0.143 = 3.932 \text{ a. u.}$$

Such a result gives, for the quadrupole coupling constant, the value $e^2qQ = 72.9 \text{ MH}$, in good agreement with the assumed experimental value*.

To separate the various contributions of the molecular orbitals of the inner shells from those of the valence shell, let us refer to the matrix \mathbf{C} reported in Tab. 2.

Such a matrix has been calculated by diagonalizing the Fock's \mathbf{F} matrix, which had been obtained from the \mathbf{R} matrix of the system. The two orbitals φ^b and φ^{nb} are the following linear combinations:

$$\begin{aligned} \varphi^b &= 0.473218 \varphi_{4\sigma} + 0.880945 \varphi_{5\sigma} \\ \varphi^{nb} &= 0.880945 \varphi_{4\sigma} - 0.473218 \varphi_{5\sigma} \end{aligned}$$

* The quadrupole coupling constant of gaseous HCl³⁵ is not known, but there is good reason to believe that its value is very close to that of gaseous DCI³⁵, which amounts to 67.3 MH [7].

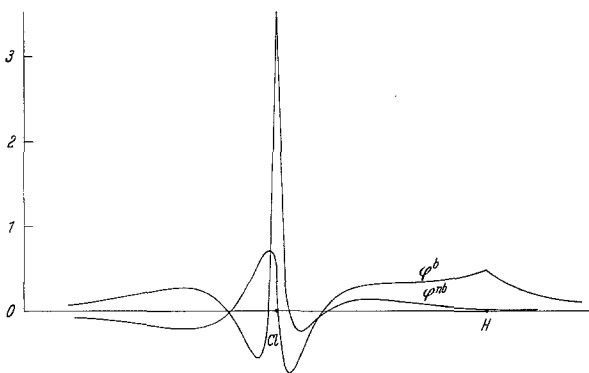


Fig. 1
Bonding and lone pair orbitals for HCl, along the internuclear axis

Table 2. *Molecular orbitals for HCl and Cl⁻*

	$\varphi_{1\sigma}$	$\varphi_{2\sigma}$	$\varphi_{3\sigma}$	φ^b	φ^{nb}	$\varphi_{1\pi}, \varphi_{1\pi}^-$	$\varphi_{2\pi}, \varphi_{2\pi}^-$
h	0.00011	-0.00430	-0.00273	-0.52557	0.00065		
p	0.00031	-0.01744	-0.00696	-0.04993	-0.00684		
$1s$	-0.98923 0.98923	0.32065 0.32083	-0.00470	-0.01254	-0.09150		
$2s$	-0.02604 0.02599	-0.26299 -0.26475	0.00512	0.00825	0.04627		
2σ	0.00996 -0.00987	-0.91454 -0.91161	0.01101	0.07009	0.40699		
$3s$	-0.00361 0.00345	0.22769 0.21967	-0.00088	-0.09986	-0.98661		
3σ	0.00131 -0.00132	-0.08721 0.08767	0.00213	0.08842	-0.17552		
$2z$	-0.00024	-0.00261	-0.50080 -0.50302	0.09804	-0.03102		
2ξ	0.00025	-0.01502	-0.58176 -0.57901	0.15235	-0.03588		
$3z$	-0.00026	0.01142	0.07092 0.06832	-0.49223	0.12745		
3ξ	0.00004	-0.00158	-0.02434 -0.02510	-0.24368	0.14082		
$2x$						0.50349	-0.12807
2ξ						0.57855	-0.17719
$3x$						-0.06830	0.60161
3ξ						0.02495	0.53581
e_{zz}^{HCl}	0	-0.025	-158.601	-6.589	-0.545	-79.634	5.141

which have been obtained by an orthogonal transformation of the delocalized orbitals $\varphi_{4\sigma}$ and $\varphi_{5\sigma}$ of Ref. [7]. This transformation has been chosen in such a way to minimize the contributions of the h and p orbitals centered on the H atom in the φ^{nb} function, and therefore reduces the φ^{nb} itself to a "quasi" atomic orbital (see Fig. 1). The conclusions which we will arrive in the present work, can also be reached by using other localization methods, such as that of the "exclusive orbitals" proposed by FORSTER and BOYS [2]. In the same Tab. 2 are also shown (in

italics) for the purpose of comparison, the analogous coefficients relative to the inner shells of the Cl^- ion. In the last row of the table the contributions of the various molecular orbitals of HCl to the field gradient are reported.

The comparison between the coefficients of the correspondent orbitals of Cl^- and of HCl supports the partition of the orbitals of the latter in a core group ($1\sigma, 2\sigma, 3\sigma, 1\pi, 1\bar{\pi}$) and a valence shell group ($b, nb, 2\pi, 2\bar{\pi}$).

The electronic part of eq. (1) can therefore be written in the form:

$$(eq)_{el} = \sum_j \left[\sum_r \sum_s 2 c_{rj} c_{sj} (eq)_{rs} \right] + \sum_k \left[\sum_r \sum_s 2 c_{rk} c_{sk} (eq)_{rs} \right] \quad (2)$$

in which the index j refers to the core orbitals and the index k to those of the valence shell.

In case that no polarisation effect nor any participation of the internal shells to the bond exist, the "core" contribution to $(eq)_{el}$ would be zero. Actually, as it can be seen from the last row of Tab. 2, this contribution rises up to the value $+0.642$ a. u., *i. e.* the 17% of the total.

It is useful to evidence the flexibility of the molecular orbitals which is allowed by the large number of basic functions, by rewriting the valence shell orbitals in a more compact form:

$$\begin{aligned} \varphi^b &= 0.07084 S^b + 0.63967 P_z^b + 0.52794 H^b \\ \varphi^{nb} &= 0.96974 S^{nb} - 0.23809 P_z^{nb} - 0.00686 H^{nb} \\ \varphi_{2\pi} &= P_\pi \end{aligned} \quad (3)$$

According to eq. (3), in any molecular orbital, the contributions of the basic functions of Cl are grouped in single terms, according to their quantum number l , while the contribution of the basic functions centered on the H atom are grouped in the last term. The functions S , P and H , in equations (3) are normalized and retain the angular properties and the origin of the basic functions; their explicit expressions are:

$$\begin{cases} S^b = 0.17705 (1s) - 0.11641 (2s) - 0.98942 (2\sigma) + 1.40975 (3s) \\ \quad \quad \quad - 1.24819 (3\sigma) \\ P_z^b = -0.15327 (2z) - 0.23816 (2\xi) + 0.76951 (3z) + 0.38095 (3\xi) \\ H^b = 0.99552 (h) + 0.09458 (p) \end{cases} \quad (4)$$

$$\begin{cases} S^{nb} = 0.09435 (1s) - 0.04771 (2s) - 0.41969 (2\sigma) + 1.01740 (3s) \\ \quad \quad \quad + 0.18099 (3\sigma) \\ P_z^{nb} = -0.13028 (2z) - 0.15072 (2\xi) + 0.53533 (3z) + 0.59147 (3\xi) \\ H^{nb} = 0.09468 (h) - 0.99855 (p) \end{cases}$$

$$P_\pi = -0.12807 (2x) - 0.17719 (2\xi) + 0.60161 (3x) + 0.53581 (3\xi).$$

It can be seen, by inspections of equations (4), that the formation of the molecule causes a different modification of the same function in the various orbitals. As an example, the radial parts of the functions P_z^b and P_z^{nb} are reported in Fig. 2.

By utilizing the valence shell orbitals in the form (3) the second term of eq. (2) can be written as:

$$(eq)_{v.s.} = \sum_k \left[\sum_r \sum_s 2 a_{rk} a_{sk} (eq)_{rs}^k \right], \quad (5)$$

where the a_{rk} 's are the coefficients of the functions (3) while the values of the $(eq)_{rs}^k$ depend on the k -th molecular orbital being considered, and can easily be calculated from the coefficients of eq. (4).

The numerical values of the contributions to $(eq)_{v.s.}$ are written below in Tab. 3 and 4.

Table 3				Table 4				
φ^b	S^b	P_z^b	H^b	φ^{nb}	S^{nb}	P_z^{nb}	H^{nb}	
The corresponding values of $a_{rk}a_{sk}$ and of $(eq)_{rs}^k$ are also reported in the sequence:	S^b	0.00502	0.04531	0.03740	S^{nb}	0.94039	-0.23088	-0.00665
		0	0	0.02128		0	0	0.05972
		0	0	0.00159		0	0	-0.00079
$a_{rk} a_{sk}$ $(eq)_{rs}^k$ $2 a_{rk} a_{sk} (eq)_{rs}^k$	P_z^b	0.04531	0.40917	0.33771	P_z^{nb}	-0.23088	0.05668	0.00163
		0	-7.89044	-0.04196		0	-4.79659	0.04596
		0	-6.45683	-0.02834		0	-0.54379	0.00015
H^b		0.03740	0.33771	0.27872	H^{nb}	-0.00665	0.00163	0.00005
		0.02128	-0.04196	-0.14070		0.05972	0.04596	-0.21277
		0.00159	-0.02834	-0.07843		-0.00079	0.00015	-0.00002

These tables show that the contribution of the overlap terms is very small: about two orders of magnitude smaller than the dominant terms; the contribution of the terms $H-H$ is also small and it partially compensates that of opposite sign

generated by the proton. The sum of the two amounts to 0.06 a. u. and represents 1.5% of the overall electric field gradient.

The most important terms are those of $P-P$ type, which, because of the particular sensitivity of the field gradient to the form of the functions in the vicinity of the nucleus, are very different from each other:

$$\begin{aligned} eq_P^b &= -7.89 \\ eq_P^{nb} &= -4.80 \\ 2 eq_P^n &= 5.14 \end{aligned} \quad (6)$$

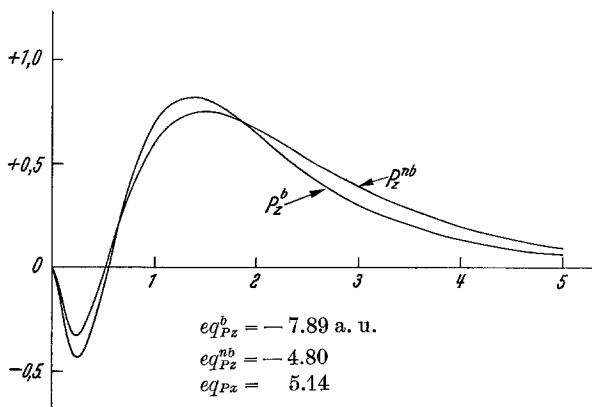


Fig. 2. P_z^b and P_z^{nb} functions for HCl [$P = r R(r)$]

This result shows, at least partially, the limit of the semi empirical treatment, which assumes that the contributions of the P functions to the field gradient are all equal, and carries out the calculation only on the basis of the occupation numbers of these functions*.

We may conclude that perhaps the two following results may constitute a good basis for improving the prevision of the quadrupole coupling constant of other chlorine-containing molecules:

- a) the inner shell does not completely retain their spherical symmetry,

* Analogous differences in the values of eq for the σ and π orbitals of the N_2 molecule has already been well evidenced by RICHARDSON [6].

b) the functions P_z^b , P_z^{nb} and P_π which enter the molecular orbitals of the valence shell do not give exactly equal contributions to the field gradient, neither equal to that of the correspondent $3p$ functions of the isolated atom.

Appendix

Perhaps, it is worthwhile, on the basis of the previously discussed results, to repeat the calculation according to the classical scheme. In this scheme the quadrupole coupling constant for the molecule is:

$$(e^2qQ)_{\text{mol}} = f(e^2qQ)_{\text{at}} \quad (7)$$

where f is a factor dependent on the electronic structure of the molecule [3].

To this purpose we may rewrite eq (3) in a different form, in which the chlorine-centered functions in the σ -type orbitals, are collected as sp hybrids, with hybridization coefficients α and β respectively:

$$\varphi^b = \frac{(\alpha S^b + \sqrt{1-\alpha^2} P_z^b)_{\text{Cl}} + iH^b}{(1+i^2+2i\Delta_{\text{ClH}})^{1/2}} \quad (8a)$$

$$\begin{aligned} \varphi^{nb} &= aS^{nb} + bP_z^{nb} + cH^{nb} \\ &\simeq \sqrt{1-\beta^2} S^{nb} - \beta P_z^{nb} \end{aligned} \quad (8b)$$

$$\varphi_{2\pi} = P_\pi \quad (8c)$$

In eq (8b) the small contribution of the orbital H^{nb} , centered on the hydrogen atom, has been neglected [in fact, from eq (3b) one has: $a^2 + b^2 = 0.997$ instead of 1]. It may be noted that the φ^{nb} function thus simplified is still orthogonal to φ^b within 0.001*.

In eq (8a) Δ_{ClH} is the overlap integral between the bonding sp hybrid of Cl and the function H^b .

We may write:

$$(e^2qQ)_{\text{mol}} = \left\{ \frac{n_x + n_y}{2} (eq_P^x) - [n_z^b (eq_P^b) + n_z^{nb} (eq_P^{nb})] \right\} \frac{(e^2qQ)_{\text{at}}}{(eq)_{\text{at}}}, \quad (9)$$

therefore the factor f (due to the external shell) can be written as:

$$f = \frac{n_x + n_y}{2} \frac{eq_P^x}{(eq)_{\text{at}}} - \left[n_z^b \frac{eq_P^b}{(eq)_{\text{at}}} + n_z^{nb} \frac{eq_P^{nb}}{eq_{\text{at}}} \right]. \quad (10)$$

From eqs (8) one has, more explicitly:

$$f = 2 \frac{eq_P^x}{(eq)_{\text{at}}} - \left[\frac{(1-\alpha^2)(1+I)}{1+\Delta_{\text{ClH}}(1-I^2)} \frac{eq_P^b}{(eq)_{\text{at}}} + 2\beta^2 \frac{eq_P^{nb}}{(eq)_{\text{at}}} \right], \quad (11)$$

where

$$I = \frac{1-i^2}{1+i^2}.$$

In these relations the rather small contributions of the overlap charges have been neglected and the partial compensation between electronic and nuclear charges of the H atom has been utilized.

By taking $(eq)_{\text{at}} = (e^2qQ)_{\text{at}}/eQ \sim 5.92$ a. u. and recalling equations (3) and (6) we obtain for the valence shell electrons, $f = 0.55$ a. u.**. To this value, the contributions of the inner shells electrons, amounting to $0.642/5.92 \sim 0.11$ a. u., must be added.

The overall value of f is then 0.66, practically equivalent to the value which can be deducted from eq. (1), against the experimental value of 0.61.

* In the simplified scheme of TOWNES and DAILEY's theory [8] the σ -type lone-pair orbital of chlorine is usually taken orthogonal to the sp hybrid of the bonding function. As it is well known this is only a first approximation. It is easily seen that between the hybrids contained in the orbitals φ^b and φ^{nb} there is a lack of orthogonality of about 0.225.

** For the values of $(e^2qQ)_{\text{at}}$ and of eQ see, for instance, ref. [3] p. 282 and 338.

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