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Optimization of the Basis Functions in SCF MO Calculations Optimized One-Center SCF MO Basis Set for HCl

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Equations have been derived which give the first derivatives of the energy, calculated by the expansion SCF MO method, with respect to the parameters contained in the basis functions. The amount of computations needed has a reasonable limit and is particularly reduced if the parameters are the orbital exponents of STO basis functions. Knowledge of such derivatives has been exployted to optimize a one center basis set, comprised of 71 STO functions, for a SCF MO wave function of HCl. A molecular energy of −460.05810 au has been obtained at a bond length of 2.424 au. The resulting wave function, has been used to calculate several observables of interest.

Des équations ont été établies donnant les dérivées premières de l'énergie par rapport aux paramètres des fonctions de la base utilisée dans la méthode SCF MO. La quantité de calculs nécessaire est raisonnablement bornée; elle est particulièrement réduite s'il s'agit des exposants orbitaux des fonctions de base de Slater. La connaissance de ces dérivées a été utilisée pour optimiser une base à un centre, comprenant 71 orbitales de Slater, pour la fonction d'onde SCF MO de HCl. L'énergie moléculaire obtenue est −460.05810 u.a. pour une longueur de liaison de 2.424 a.u. La fonction d'onde résultante a été utilisée pour le calcul de plusieurs observables intéressantes.

Ausdrücke für die ersten Ableitungen der SCF-Energie nach den in den Basis-Funktionen enthaltenen Parametern werden abgeleitet. Die zusätzlichen Rechnungen sind gering, wenn die Parameter die Orbitalexponenten von Slater-Funktionen sind. Die Kenntnis solcher Ableitungen wird dazu ausgenutzt, eine Einzentren-Basis von Slater-Funktionen für eine SCF-Wellenfunktion des HCl-Moleküls zu optimieren. Die elektronische Molekül-Energie ergab sich zu −460.05810 AE bei einem Kernabstand von 2.424 AE. Mehrere bedeutsame Erwartungswerte wurden berechnet.

Introduction

In SCF MO calculations by the expansion method the linear parameters are fully optimized by the Roothaan procedure [*15*], but, as widely recognized [*1*, *2*], the optimization of the non-linear parameters is of paramount importance when, as is practically always the case, the basis set is comprised of a limited number of functions.

Unfortunately there is no general method available to perform this optimization, and the commonly applied techniques [*16*, *18*] are more or less based upon brute force methods which involve a great amount of calculations.

A first step toward a more systematic and convenient approach to the problem consists in evaluating the derivatives of the calculated energy with respect to those non-linear parameters which are to be optimized. Knowledge of such derivatives permits either the elaboration of some systematic procedure based, for instance, upon the steepest descent method, or upon a reasonable guess of the variations to be applied to the non-linear parameters.

In the next section it will be shown that the evaluation of these derivatives is not difficult for SCF MO wave functions and the formulae become particularly convenient, from a computational viewpoint, if the non-linear parameters are the orbital exponents of STO basis functions.

Finally, a OCE SCF MO [*10*] wave functions for HCl is presented which was optimized with respect to the orbital exponents of the STO basis functions.

Derivation of the Equations

Here, for the sake of simplicity, closed shell cases and real basis functions are considered.

Let us suppose we have a basis set $\{\chi\}$ of dimension n and that each χ_i contains an adjustable parameter α_i. With this basis an SCF MO wave function may be calculated by the Roothaan procedure, which for the system under consideration and with a particular choice of the α's affords an estimate of the energy E. This energy is given [*17*] by

$$E = [2\boldsymbol{H} + \boldsymbol{P}\,\boldsymbol{D}]^{\dagger}\,\boldsymbol{D} \tag{1}$$

where

$$H_{ij} = \langle \chi_i \mid h \mid \chi_j \rangle \tag{2a}$$

$$P_{ij}^{kl} = 2\,\langle \chi_i\,\chi_k \mid \chi_j\,\chi_l \rangle - \tfrac{1}{2}\,[\langle \chi_i\,\chi_k \mid \chi_l\,\chi_j \rangle + \langle \chi_i\,\chi_l \mid \chi_k\,\chi_j \rangle] \tag{2b}$$

$$D_{kl} = \sum_s C_{ks}\,C_{ls}(2 - \delta_{kl})\,. \tag{2c}$$

H_{ij} is the matrix element of the one-electron part $\boldsymbol{h}$ of the hamiltonian; $\boldsymbol{P}_{ij}^{kl}$ is one element of symmetrized supermatrix $\boldsymbol{P}$ while D_{kl} are the elements of the density matrix. The couples of indices i, j (k, l) include all possible values without repetition arranged in a dictionary order.

The self consistent vectors $\boldsymbol{C}_{\cdot s}$ satisfy the equations

$$(\boldsymbol{H} + \boldsymbol{P}\,\boldsymbol{D})\,\boldsymbol{C}_{\cdot s} = \varepsilon_s\,\boldsymbol{S}\,\boldsymbol{C}_{\cdot s} \tag{3}$$

$$\boldsymbol{C}_{\cdot s}^{\dagger}\,\boldsymbol{S}\,\boldsymbol{C}_{\cdot p} = \delta_{sp} \tag{4}$$

where $\boldsymbol{S}$ is the overlap matrix.

If all the quantities appearing in the Eqs. (1), (2) and (3) are analytical functions of the parameters α's, it is possible to differentiate Eqs. (1) and (4) with respect to one of them, thereby obtaining

$$\frac{\partial E}{\partial \alpha_m} = \left\{\left[2\frac{\partial \boldsymbol{H}}{\partial \alpha_m} + \frac{\partial \boldsymbol{P}}{\partial \alpha_m}\boldsymbol{D} + \boldsymbol{P}\,\frac{\partial \boldsymbol{D}}{\partial \alpha_m}\right]^{\dagger}\boldsymbol{D} + [2\boldsymbol{H} + \boldsymbol{P}\,\boldsymbol{D}]^{\dagger}\,\frac{\partial \boldsymbol{D}}{\partial \alpha_m}\right\} \tag{5}$$

$$\frac{\partial \boldsymbol{C}_{\cdot s}^{\dagger}}{\partial \alpha_m}\boldsymbol{S}\,\boldsymbol{C}_{\cdot p} + \boldsymbol{C}_{\cdot s}^{\dagger}\,\boldsymbol{S}\,\frac{\partial \boldsymbol{C}_{\cdot p}}{\partial \alpha_m} + \boldsymbol{C}_{\cdot s}^{\dagger}\,\frac{\partial \boldsymbol{S}}{\partial \alpha_m}\boldsymbol{C}_{\cdot p} = 0\,. \tag{6}$$

Since

$$[\boldsymbol{P}\cdot\boldsymbol{D}]^{\dagger}\,\frac{\partial \boldsymbol{D}}{\partial \alpha_m} = \left[\boldsymbol{P}\cdot\frac{\partial \boldsymbol{D}}{\partial \alpha_m}\right]^{\dagger}\boldsymbol{D}$$

Eq. (5) becomes

$$\frac{\partial E}{\partial \alpha_m} = \left\{\left[2\frac{\partial \boldsymbol{H}}{\partial \alpha_m} + \frac{\partial \boldsymbol{P}}{\partial \alpha_m}\boldsymbol{D}\right]^{\dagger}\boldsymbol{D} + 2\,[\boldsymbol{H} + \boldsymbol{P}\boldsymbol{D}]^{\dagger}\,\frac{\partial \boldsymbol{D}}{\partial \alpha_m}\right\}. \tag{7}$$

The last equation contains the derivative of the density matrix which is rather difficult to evaluate. Fortunately this term can be eliminated by means of the following considerations. According to Eq. (2c)

$$\frac{\partial D_{kl}}{\partial \alpha_m} = \sum_s \left(\frac{\partial C_{ks}}{\partial \alpha_m} C_{ls} + C_{ks} \frac{\partial C_{ls}}{\partial \alpha_m} \right) (2 - \delta_{kl}) . \tag{8}$$

Substituting this relation into Eq. (7) and using Eq. (3) and (6) results in the following

$$\frac{\partial E}{\partial \alpha_m} = \left\{ \left[2 \frac{\partial \boldsymbol{H}}{\partial \alpha_m} + \frac{\partial \boldsymbol{P}}{\partial \alpha_m} \boldsymbol{D} \right]^{\dagger} \boldsymbol{D} - 2 \left[\frac{\partial \boldsymbol{S}}{\partial \alpha_m} \right]^{\dagger} \boldsymbol{B} \right\} . \tag{9}$$

$\boldsymbol{B}$ is used to designate a supervector whose elements are given by

$$B_{ij} = \sum_s \varepsilon_s C_{is} C_{js} (2 - \delta_{ij}) . \tag{10}$$

Eq. (9) demonstrates that the derivatives of the self-consistent energy with respect to the parameters α's are expressible simply by means of the derivative of the basic integrals which explicitly depend upon the α's. To obtain a workable expression it is convenient to define the new matrices $\boldsymbol{H}^I$, $\boldsymbol{H}^{II}$, $\boldsymbol{S}^I$, $\boldsymbol{S}^{II}$, $\boldsymbol{P}^I$, $\boldsymbol{P}^{II}$, $\boldsymbol{P}^{III}$ and $\boldsymbol{P}^{IV}$. The superscript indicates that these matrices are obtained from the $\boldsymbol{H}$, $\boldsymbol{S}$ and $\boldsymbol{P}$ matrices simply taking the derivative of each element with respect to the parameter α of the first, second, third or fourth functions. The ordering of the functions runs according to the convention: first, second, third and fourth functions correspond to the lower left, lower right, upper left and upper right indices. For instance

$$P_{ij}^{III\,kl} = \frac{\partial}{\partial \alpha_k} P_{ij}^{kl} . \tag{11}$$

By these definitions, Eq. (9) written in detail becomes

$$\begin{aligned} \frac{\partial E}{\partial \alpha_m} = {} & \sum_{i \leq j} \{ 2 [H_{ij}^I \delta_{im} + H_{ij}^{II} \delta_{jm}] + \sum_{k \leq l} [P_{ij}^{I\,kl} \delta_{im} + P_{ij}^{II\,kl} \delta_{jm} + \\ & + P_{ij}^{III\,kl} \delta_{km} + P_{ij}^{IV\,kl} \delta_{jm}] D_{kl} \} D_{ij} - 2 \sum_{i \leq j} [S_{ij}^I \delta_{im} + S_{ij}^{II} \delta_{jm}] D_{ij} . \end{aligned} \tag{12}$$

Exploiting the symmetry properties of the exchange of the indices of the elements of the $\boldsymbol{H}$, $\boldsymbol{S}$, $\boldsymbol{P}$ matrices, reduces eq. (12) to

$$\begin{aligned} \frac{\partial E}{\partial \alpha_m} = 2 \sum_{i \leq j} \Bigg\{ & \left[\left(H_{ij}^I + \sum_{k \leq l} P_{ij}^{I\,kl} D_{kl} \right) D_{ij} - S_{ij}^I B_{ij} \right] \delta_{im} + \\ & + \left[\left(H_{ij}^{II} + \sum_{k \leq l} P_{ij}^{II\,kl} D_{kl} \right) D_{ij} - S_{ij}^{II} B_{ij} \right] \delta_{jm} \Bigg\} . \end{aligned} \tag{13}$$

Finally upon defining the matrices $\boldsymbol{G}^I = \boldsymbol{P}^I \boldsymbol{D}$ and $\boldsymbol{G}^{II} = \boldsymbol{P}^{II} \boldsymbol{D}$, Eq. (13) can be written as

$$\begin{aligned} \frac{\partial E}{\partial \alpha_m} = 2 \Bigg\{ & \sum_{i=1}^{m} (\boldsymbol{H}^{II} + \boldsymbol{G}^{II})_{im} D_{im} - S_{im}^{II} B_{im}] + \\ & + \sum_{j=m}^{n} [(\boldsymbol{H}^I + \boldsymbol{G}^I)_{mj} D_{mj} - S_{mj}^I B_{mj}] \Bigg\} . \end{aligned} \tag{14}$$

This last equation makes it evident that for purposes of evaluating all the first derivatives, $\partial E / \partial \alpha_m$, it is necessary to evaluate two more one-electron matrices and two more two-electron supermatrices.

STO basis set

A particularly convenient expression is obtained if the parameters α are the orbital exponents ζ of a STO basis set. A STO $\chi_{N,L,M}(\zeta;\bar{r})$ is defined as

$$\chi_{N,L,M}(\zeta;\bar{r}) = \left[\frac{(2\,\zeta)^{2N+1}}{(2\,N)!}\right]^{1/2} r^{N-1}\, e^{-\zeta r}\, S_{L,M}(\vartheta,\varphi) \tag{15}$$

where $S_{L,M}$ is a real spherical harmonic. In the case of the matrix elements of the $\boldsymbol{H}$, $\boldsymbol{S}$ and $\boldsymbol{P}$ matrices it is legitimate to perform the differentiation under the integral sign. Since

$$\frac{\partial}{\partial\zeta}\chi_{N,L,M} = \frac{N+\frac{1}{2}}{\zeta}\chi_{N,L,M} - r\,\chi_{N,L,M} \tag{16}$$

it is clear that each element of the $\boldsymbol{H}^{I}$, $\boldsymbol{H}^{II}$, $\boldsymbol{S}^{I}$, $\boldsymbol{S}^{II}$, $\boldsymbol{P}^{I}$ and $\boldsymbol{P}^{II}$ matrices will be given by a sum of two terms. The first one is equal to the original element times the factor $(N+\frac{1}{2})/\zeta$ corresponding either to the first or to the second function. The second one differs from the original one only because the power of r of the first or of the second function has been raised by one.

For instance

$$H^{II}_{mj} = \frac{N_j+\frac{1}{2}}{\zeta_j} H_{mj} - \langle \chi_m \,|\, h\, |r\chi_j\rangle\,. \tag{17}$$

If these last matrices are indicated by $\boldsymbol{H}^{I'}$, $\boldsymbol{H}^{II'}$, $\boldsymbol{S}^{I'}$, $\boldsymbol{S}^{II'}$, $\boldsymbol{P}^{I'}$ and $\boldsymbol{P}^{II'}$ Eq. (14) becomes

$$\begin{aligned}\frac{\partial E}{\partial \zeta_m} = 2\,\frac{N_m+\frac{1}{2}}{\zeta_m}&\left\{\sum_{i=1}^{m}[(\boldsymbol{H}+\boldsymbol{G})_{im}\,D_{im} - S_{im}\,B_{im}] + \right.\\ &\left.+\sum_{j=m}^{n}[(\boldsymbol{H}+\boldsymbol{G})_{mj}\,D_{mj} - S_{mj}\,B_{mj}]\right\} + 2\left\{\sum_{i=1}^{m}[(\boldsymbol{H}^{II'}+\boldsymbol{G}^{II'})_{im}\,D_{im} + \right.\\ &\left.- S^{II'}_{im}\,B_{im}] + \sum_{j=m}^{n}[(\boldsymbol{H}^{I'}+\boldsymbol{G}^{I'})_{mj} - S^{I'}_{mj}\,B_{mj}]\right\}\end{aligned} \tag{18}$$

where the meaning of $\boldsymbol{G}^{I'}$ and $\boldsymbol{G}^{II'}$ is evident from the previous definitions.

By using Eqs. (2c), (10), (3) and (4) it is not difficult to see that the first term on the right of Eq. (18) vanishes, giving

$$\begin{aligned}\frac{\partial E}{\partial \zeta_m} = 2&\left\{\sum_{i=1}^{m}[(\boldsymbol{H}^{II'}+\boldsymbol{G}^{II'})_{im}\,D_{im} - S^{II'}_{im}\,B_{im}] + \right.\\ &\left.+\sum_{j=m}^{n}[(\boldsymbol{H}^{I'}+\boldsymbol{G}^{I'})_{mj}\,D_{mj} - S^{I'}_{mj}\,B_{mj}]\right\}.\end{aligned} \tag{19}$$

This last equation represents a convenient working formula. It requires the computation of two more one-electron matrices and two more two-electron matrices, the values of whose elements are readily obtained once we have the means for evaluating the original basic integrals.

In fact, making slight modifications to the programs used to compute the basic integrals, it is possible to carry out simultaneously the evaluation of the modified integrals with very little increase in computational time. Naturally the convenience of these modifications will depend upon the particular technique used to evaluate the more troublesome integrals, but there are no basic difficulties involved.

In addition, all the factorization and therefore all the organization of the SCF program can be retained to compute Eq. (19).

Optimized OCE SCF MO for HCl

The evaluation of the derivative of the energy with respect to the orbital exponents of STO basis functions has been included in a program written for a Bendix G 20 Computer.

By the use of this program a one center basis set SCF MO's wave function for HCl has been computed and optimized with respect to the orbital exponents ζ. The relevant results including the expectation values of the field gradient at the Cl nucleus and of some electrical multipole moments are here reported.

The optimization of the basis functions, which are all located upon the Cl nucleus, has been carried out by the following scheme: starting with a limited basis set, which was taken to be equal to that used elsewhere (11) plus a few functions of *s* and *p* type, the optimization of the ζ's of such a basis was carried out manually by a steepest descent criterion.

Table 1. *Electronic energy derivatives with respect to the orbital exponents of an intermediate limited basis*

σ type					π type				
n	l	m	ζ	$\partial E_e/\partial\zeta(10^{-2}$ au)	n	l	m	ζ	$\partial E_e/\partial\zeta(10^{-2}$ au)
1	0	0	23.990	0.0166	2	1	1	8.890	−1.2953
1	0	0	15.305	−0.0476	2	1	1	5.810	1.3612
1	0	0	10.000	−0.0016	3	1	1	4.290	−0.5833
2	0	0	8.502	−0.0138	3	1	1	2.350	0.1088
2	0	0	6.297	0.0457	3	1	1	1.180	−1.0118
2	0	0	4.000	0.0040	3	1	1	0.510	−0.2661
3	0	0	1.767	0.0340	3	2	1	1.700	0.0030
3	0	0	1.404	0.0132	3	2	1	1.102	−0.0106
3	0	0	0.805	−0.0089	4	2	1	1.200	0.0085
4	0	0	2.067	−0.1450	4	3	1	1.600	−0.0015
2	1	0	8.790	−1.3857	4	3	1	1.100	−0.0007
2	1	0	5.820	1.4349					
3	1	0	4.350	−0.5886					
3	1	0	2.000	−0.4093					
3	1	0	1.220	−0.2281					
3	1	0	0.860	−0.1880					
3	2	0	2.224	0.0691					
3	2	0	1.492	0.0225					
4	2	0	1.493	0.0383					
4	3	0	1.615	−0.6563					
4	3	0	2.125	0.02752					

$R_{\mathrm{HCl}} = 2.34$ au; $E_{el} = -467.24609$ au; $E_{tot} = -459.98113$ au

The variations $\Delta\zeta_m$ were therefore chosen to be proportional to the derivatives $\partial E/\partial\zeta_m$. The proportionality constant was chosen at each step according to the previous trend in order to avoid overshooting.

As a general rule for this case and other cases as well, it was found that a proportionality constant K given by

$$K = -\left\{a + b\left[\sum_i (\partial E/\partial\zeta_i)^2\right]^{1/2}\right\}^{-1} \tag{20}$$

Table 2. *Results for* HCl *with the extended basis*

				$R_{HCl} = 2.424$		$E_{el} = -467.07130$		$E_{tot} = -460.05810$
				Coefficients				
n	l	m	ζ	1σ	2σ	3σ	4σ	5σ
1	0	0	23.980	0.09166	0.00189	−0.00003	−0.02578	0.00897
1	0	0	15.305	1.07967	−0.20587	0.00098	0.27135	−0.09095
1	0	0	10.000	−0.22474	−0.22100	0.00074	−0.24859	0.09151
2	0	0	8.502	0.11990	0.11237	0.00017	0.56940	−0.19886
2	0	0	6.297	−0.06529	0.93843	−0.00566	−1.18487	0.38862
2	0	0	4.000	0.01557	0.11949	0.00130	0.57420	−0.19952
3	0	0	1.767	−0.00284	−0.00770	0.00050	1.02584	−0.24753
3	0	0	1.104	−0.00159	−0.00508	−0.00005	0.17500	−0.09601
3	0	0	0.805	0.00073	0.00233	0.00000	−0.10227	0.06199
9	0	0	3.419	0.00264	0.00803	−0.00012	−0.32499	0.20646
2	1	0	8.885	0.00021	0.00059	0.31653	−0.01056	−0.04967
2	1	0	5.725	−0.00022	0.00249	0.63172	−0.01773	−0.19011
3	1	0	4.361	0.00011	0.00082	0.11804	−0.00486	0.08679
3	1	0	2.004	−0.00004	0.00017	−0.02183	0.12564	0.54599
3	1	0	1.222	−0.00004	−0.00024	−0.02286	−0.00885	0.61500
3	1	0	0.862	0.00001	0.00007	0.00622	0.00370	−0.17441
9	1	0	3.419	0.00004	0.00022	0.02737	0.05752	−0.08456
3	2	0	2.224	0.00001	0.00423	0.00371	−0.00019	0.06836
3	2	0	1.492	−0.00002	−0.00717	−0.00580	0.07935	0.05115
6	2	0	2.137	0.00001	0.00332	0.00260	−0.05934	0.02405
9	2	0	3.419	0.00000	0.00081	0.00076	0.07764	0.13177
4	3	0	1.675	0.00000	−0.00006	0.00018	−0.04105	−0.01571
4	3	0	2.125	0.00000	0.00024	0.00070	0.03780	0.03370
9	3	0	3.419	0.00000	0.00001	−0.00059	0.06759	0.11942
5	4	0	2.000	0.00000	0.00020	0.00023	−0.00107	−0.01311
9	4	0	3.419	0.00000	−0.00011	−0.00008	0.04053	0.09389
6	5	0	2.136	0.00000	−0.00004	−0.00006	−0.02374	−0.03729
9	5	0	3.419	0.00000	0.00010	0.00015	0.04760	0.08541
7	6	0	2.564	0.00000	−0.00004	−0.00002	−0.03322	−0.05715
9	6	0	3.419	0.00000	0.00007	0.00008	0.04877	0.08771
9	7	0	3.419	0.00000	0.00002	0.00004	0.01113	0.02175
Orbital energies (au)				−104.85153	−10.57766	−8.03915	−1.12047	−0.62171

				Coefficients	
n	l	m	ζ	$1\pi_x$	$2\pi_x$
2	1	1	8.990	0.30703	−0.07154
2	1	1	5.720	0.64523	−0.19524
3	1	1	4.330	0.12233	0.01423
3	1	1	2.340	−0.05300	0.67714
3	1	1	1.270	0.06102	0.43384
6	1	1	2.137	−0.07671	0.03839
9	1	1	3.419	0.04082	−0.06366
3	2	1	1.700	−0.02731	0.02735
3	2	1	1.100	0.09636	−0.01801
4	2	1	1.200	−0.06315	0.01925
7	2	1	2.564	−0.01247	0.01127

				Coefficients	
n	l	m	ζ	$1\pi_x$	$2\pi_v$
4	3	1	1.600	0.00112	0.02340
4	3	1	1.100	−0.00010	−0.00454
7	3	1	2.564	−0.00099	0.00311
5	4	1	1.500	−0.00003	0.00062
9	4	1	3.419	0.00006	0.00989
6	5	1	2.136	−0.00000	−0.00070
9	5	1	3.419	0.00003	0.00694
8	6	1	2.990	0.00001	0.00382
9	7	1	3.419	0.00001	0.00234
Orbital energies (au)				−8.03815	−0.48078

was convenient. The numerical value of a was ~0.3 and of b ~2.0. By this method with 7 to 8 iterations, all derivatives were reduced to the order of magnitude of 10^{-2} or less.

Tab. 1 reports the results obtained, after a few iterations, for the limited starting basis comprised of 43 STO functions. The calculation refers to an interatomic distance of 2.34 au, and a SCF total energy of -459.98113 au was obtained. This value of the energy compares favorably with other calculations where more usual polycentric basis sets were employed (12, 19).

It is necessary to point out that the described optimization was carried out by neglecting the dependence of the ζ's from the internuclear distance R. The whole optimization process was performed for values of R around 2.4 au. Neglect of this does not introduce serious errors because the variation of the total energy due to reasonable changes of R are smaller than the variations considered significant for the optimization.

Table 3. *Comparison of calculated quantities with experimental data*

Property	Unit	Present Results	Nesbet (12)	Experiments
R_e	(au)	2.426	2.5187	2.4085
Molecular Energy				
E_e	(au)	-460.05810	-459.80514	-462.81^{a}
$(\partial^2 E/\partial R^2)_e$	(au)	0.540	0.2308	0.332
$\langle M_{1,0}\rangle_e$	10^{-18} esu	1.357 (1.32 at $R_{e,exp}$)	1.488	1.081
$(\partial \langle M_{1,0}\rangle/\partial R)_e$	10^{-10} esu	2.065	1.718	± 0.95 *[14]*
$\langle M_{2,0}\rangle$	10^{-26} esu	4.200^{b} (4.047^{c} at $R_{e,exp}$)	3.957^{c}	5.8 ± 1.5^{c} *[21]*
$(\partial \langle M_{2,0}\rangle/\partial R)_e$	10^{-18} esu	6.697^{b}	4.538^{c}	—
$\langle M_{3,0}\rangle$	10^{-34} esu	3.704^{b}	—	—
$(\partial \langle M_{3,0}\rangle/\partial R)_e$	10^{-26} esu	15.64^{b}	—	—
$\langle M_{4,0}\rangle$	10^{-42} esu	6.653^{b}	—	—
$(\partial \langle M_{4,0}\rangle/\partial R)_e$	10^{-34} esu	29.53^{b}	—	—
$\langle r^{-5} M_{2,0}\rangle_e$	10^{-45} esu	6.068^{b} (5.95 at $R_{e,exp}$)	—	5.88^{d}
$(\partial \langle r^{-5} M_{2,0}\rangle/\partial R)_e$	10^{-23} esu	6.25^{b}	—	—

[a] As estimated in Ref. *[11]*.

[b] The origin of axes coincident with the chlorine nucleus.

[c] The origin of axes coincident with the center of mass of $^{1}H^{35}Cl$.

[d] The quadrupole moment Q of ^{35}Cl nucleus was taken to be $-0.07894 . 10^{-24}$ cm^2.

Naturally, there is no pretense being made here of presenting a set fully optimized with respect to all the relevant parameters. Once having obtained a fairly optimized limited basis set, an extended one was chosen without further optimization.

It was thought that the added STO basis functions with high l values were needed essentialy to describe the wave functions around the proton. Therefore the radial part of these functions expected to have its maximum value around $R = 2.4$. For each value of l and m, two functions were added with their radial maximum around $R = 2.4$ and with two different values of n.

By a few trials a satisfactory basis set was found. No attempt was undertaken to minimize again the ζ's, because, at this stage the basis included 71 functions, and such a minimization was considered too expensive. Tab. 2 shows the results obtained with this extended basis at an internuclear distance of 2.424 au which is very close to the value 2.426, where the interpolated minimum of the total energy was found to be.

With the above basis the SCF calculations were performed for several values of the internuclear distances and the resulting wave functions were used to obtain the expectation values of the following quantities: energy, electric dipole, quadrupole, octupole and hexadecapole moments and the field gradient at the chlorine nucleus.

A generic multipole moment operator $M_{l,m}$ is conveniently defined here as

$$M_{l,m}(r, \vartheta, \varphi) = r^l \, P_{l,|m|}(\vartheta) \begin{cases} \cos m\varphi & m \geq 0 \\ \sin m\varphi & m < 0 \end{cases} \tag{21}$$

where the $P_{l,m}$ are the associated Legendre functions [*7*].

In Tab. 3 these results and some derived quantities are reported, together with the available Nesbet's results [*12*] and experimental data.

Discussion

The calculated value of $R_e = 2.426$ appears greater than the experimental value of 2.4085 in contrast to the usual predictions made for the best single determinant wave functions [*13*]. A greater discrepancy was found by NESBET [*12*] but it is not clear whether this can be attributed to a still poor singl edeterminant wave function or to some more profound cause.

To judge the quality of the present wave function from the energy viewpoint, it is necessary to make an estimate of the HF energy. An extremly simple way to do this is to consider that the relativistic energy of HCl is identical to that of the separated atoms in their ground states and that the correlation energy of HCl is given by that of the separated atoms plus 1 eV of extra correlation due to the pairing of the *H* electron [*3*].

According to these assumptions the HF energy of HCl, $E_{HF}(\mathrm{HCl})$, is given by the sum of the HF energies of Cl [*4*] and H, minus the experimental dissociation energy, minus the zero point energy, plus 1 eV. Thus

$E_{HF}(\mathrm{HCl}) = -459.48187 - 0.5 - 0.1696 - 0.01362 + 0.03675 = -460.12835$ au. This value would establish that the present calculated value is still 0.07 au higher than the true one.

This level of accuracy does not seem to justify more speculation about the rasons why R_e calculated is greater than the experimental equilibrium distance. In addition, it is not to be forgotten that the basis was not fully optimized.

No contradiction with the prediction of [*9*] was found for the force constant. The calculated value appears to be much too large and it seems doubtful whether an optimization procedure carried out for each internuclear distance could bring substantial improvements. The situation appears to be more encouraging for the electric dipole moment, which has been greatly improved with respect to a more limited monocentric basis [*11*]. Still high is its derivative with respect to *R*, but here again it is doubtful whether a single determinant wave function is capable of giving good results for this property.

The calculated quadrupole moment of $4.200.10^{-26}$ esu agrees well with the recent determinated value of $5.8 \pm 1.5.10^{-26}$ esu (21). This was rather unepected because for all the multipole moments the nuclear contributions appear to be positive and much larger than the negative electronic contributions. Since a OCE SCF MO wave function will probably give, in these cases, an electronic contribution which is too small, the total results should be too large. It might be useful however to note that the experimental determination of the multipole moments is perhaps as delicate as their theoretical calculation.

The situation appears to be quite different for the field gradient at the chlorine nucleus. The operator involved in this case is proportional to $r^{-3} P_{2,0}$ and, therefore, will depend strongly upon the charge distribution close to the chlorine nucleus, where both the one electron approximation and the one center expansion are at their best. The calculated value of the field gradient of $5.95 . 10^{15}$ esu (for R equal to the experimental value) together with the experimental quadrupole coupling constant of gaseus ^{2}H ^{35}Cl of 67.3 Mc/sec [*5*] gives an apparent quadrupole moment for ^{35}Cl of $0.0782 . 10^{-24}$ cm^{2}. This value compares well with the experimental value of $0.07894 . 10^{-24}$ as determined from the magnetic dipole interaction and electronic quadrupole interaction constants measured from the hyperfine structure of the $^{2}P_{3/2}$ ground state [*6*, *8*].

More precisely the present calculated value should be considered an apparent value because of the polarization effect, which could modify both the electronic [*20*] and the nuclear [*22*] charge distributions. The closeness of this calculated, apparent value, to the experimental one, might be variously justified, but only actual calculation will clarify the point. The electronic polarization due to the quadrupole moment of the nucleus, which is part of the Sternheimer effect [*20*], can be calculated, within the HF scheme, by a perturbation approach.

Such a research program, which is actually under way in this laboratory, seems to be capable of giving some reliable answer for the present as well as for other cases.

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