

One-Centre-Expansion Self-Consistent-Field Calculations on HCl. Part I.

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The 71-orbital OCE-SCF calculation reported by Moccia⁸ has been repeated with electron repulsion integrals stored to greater precision: for the energy, effective field gradient, virial theorem, dipole moment, molecular quadrupole moment *etc.* the results are considerably altered and generally improved.

A series of OCE bases for HCl has been constructed by adding STO's to a basis proposed by Gilbert and Wahl for Cl₂³³. In the largest basis, 29-orbitals, the total energy —460.068938 au at the equilibrium internuclear distance is lower than that in the 71-orbital basis, —460.052595 au.

The two bases are compared with experiment and with the results from Two-Centre-Expansion theory, in order to assess their relative validity and usefulness.

INTRODUCTION

Solving the Hartree-Fock-Roothaan (HFR) equations is simplified if the basis orbitals Φ_i are centred on the same point; One Centre Expansion (OCE) wavefunctions. An OCE basis is appropriate when the molecule has high symmetry about a point and no inner-shell electrons except at the point (*e. g.* CH₄¹ or NH₃²), and when a molecular property is highly dependent on the electron distribution near one point, as in present calculations. As an OCE basis is increased, it approaches a complete set^{3,4} and can, in principle, approach the Hartree-Fock (H-F) wavefunction.

For the EFG at the Cl nucleus in HCl, the operator is $(3 \cos^2 \Theta_\alpha - 1)/r_\alpha^3$, with r_α the distance from the Cl nucleus and Θ_α the angle from the principal axis of the EFG tensor^{5,6}. This operator is large for small values of r_α , and electron density near the Cl nucleus dominates the contributions to the EFG⁷. Thus an OCE basis for HCl centred on Cl should approximate the EFG well, since a large OCE basis is flexible near its centre. An OCE calculation on HCl in a basis of 71 Slater-type orbitals (STO's) by Moccia⁸, gave an EFG agreeing with the best experimental value available at that time⁹ to within experimental uncertainty. This calculation was repeated to study the relation of the electron distribution to the EFG.

However, because in the Moccia calculation the electron repulsion integrals were stored to 6 significant figures¹⁰, while in ours they were stored to 16, the occupied MO's with higher eigenvalues, which are most sensitive

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to changes in the integrals, differed enough between the two calculations to give a difference in the EFG of 6%. A 6% difference from experimental is less than that from a two-centre double- ζ STO calculation (8% error)¹¹, but greater than that from extensive two-centre *ab-initio* STO calculations on HCl (1%—2% error)^{12,13}. Why does Moccia's basis⁸ give a less accurate EFG than two-centre bases which include fewer orbitals on Cl? How can we construct an OCE basis more accurate for the EFG? These questions are examined in later papers^{6,7,14,15}.

1. TYPES OF OCE WAVEFUNCTIONS

OCE wavefunctions fall into two classes: (i) configuration interaction wavefunctions (OCE-CI)¹⁶, (ii) molecular orbital self-consistent field (OCE-SCF) wavefunctions². Some calculations use both procedures¹⁷, with a single determinant optimized by the HFR procedure and other determinants constructed with the unoccupied HFR orbitals. The OCE-SCF method was chosen over OCE-CI for this work because to first-order the expectation value of a one-electron operator is unchanged by inclusion of CI¹⁸ except when $\langle o \rangle_e$ is nearly cancelled by $\langle o \rangle_{\text{nucl.}}$ ¹⁹, which does not occur in HCl.

2. CHARACTERISTICS OF THE OCE-SCF METHOD AND WAVEFUNCTIONS

a) Computational Advantages

Only if OCE-SCF calculations are simpler or quicker than many-centre calculations of comparable accuracy is their use justified. However all electron repulsion integrals in an OCE-SCF calculation can be evaluated quickly compared to the multicentre integrals which arise otherwise; the orbital products and r_{12}^{-1} are expressed as finite combinations of products of spherical harmonics on the expansion centre; many terms vanish upon integration over the angular coordinates²⁰; thus these integrals are evaluated much more rapidly in an OCE basis. The number of non-zero electron repulsion integrals is substantially reduced: because of the symmetry of the spherical harmonics, about 85% of the possible integrals vanish; for typical many-centre calculations this fraction is less than 50%²¹.

Another advantage arises in calculating OCE-SCF wavefunctions at a series of internuclear distances. Since $[pq | rs]$ is independent of internuclear distance if all orbitals are on the same centre, a change in internuclear distance without a change of basis requires no recalculation of the $[pq | rs]$. Some nuclear attraction integrals must be recalculated, but these are few compared to the $[pq | rs]$.

b) Limitations of the OCE-SCF wavefunction

The exact molecular electronic ψ satisfies the Schrödinger equation,

$$\left(-1/2 \sum_i \nabla_i^2 + 1/2 \sum_{i,j} (r_{ij}^{-1}) - \sum_{i,\alpha} \frac{Z_\alpha}{r_{i\alpha}} \right) \psi = E \psi, \quad (1)$$

with i, j electrons and α nuclei. At nucleus α , where $r_{i\alpha}$ vanish, ψ is multiplied by an infinite factor on the left of (1). If the ratio $H\psi/\psi$ ($\equiv E$) is to remain finite at $r_{i\alpha} = 0$, ψ must satisfy^{22,23}

$$\hat{\Delta} (\partial\psi/\partial r_{i\alpha})_{r_{i\alpha}=0} = Z_\alpha \psi(r_{i\alpha}=0), \quad (2)$$

with $\bar{\psi}$ the average of ψ over a sphere of radius $r_{i\alpha}$. (2) is the cusp condition on ψ^{24} ; for non-zero $\psi(r_{i\alpha} = 0)$, there is a discontinuity in directional derivatives of ψ through the point $r_{i\alpha} = 0^{25}$.

Consider an OCE basis composed of STO's

$$\Phi_i(n, l, m, \zeta, r, \Theta, \Phi) = N(n, \zeta) r^{n-1} \exp(-\zeta r) S_{lm}(\Theta, \Phi), \quad (3)$$

with $N(n, \zeta)$ a normalization factor and $S_{lm}(\Theta, \Phi)$ a spherical harmonic. Including STO's with $n = 1$, the OCE wavefunction satisfies (2) if α is the expansion centre, since for $n = 1$, $(\partial \Phi_i / \partial r)_{r=0} = -\zeta N(n, \zeta) S_{lm}(0, 0) \neq 0$. If α is not the expansion centre, (2) cannot be satisfied, since directional derivatives of (3) are continuous everywhere but $r = 0$. If enough basis functions are included, the OCE wavefunction can approximate a cusped function arbitrarily closely at an off-centre α .

How well does an OCE-SCF wavefunction account for the energy of attraction between the nuclei and electrons and the energy of repulsion between electrons? The potential at a point $\bar{r} = (r, \Theta, \Phi)$ due to a nucleus α is

$$V_\alpha(\bar{r}) = Z_\alpha / r_\alpha, \quad (4)$$

with Z_α the nuclear charge and r_α the distance of \bar{r} from α . $V_\alpha(\bar{r})$ can be expanded²⁶,

$$V_\alpha(\bar{r}) = 4\pi Z_\alpha \sum_{l=0}^{\infty} \frac{1}{2l+1} \frac{r^l}{r_\alpha^{l+1}} \sum_{m=-l}^l S_{lm}(\Theta_\alpha, \Phi_\alpha) S_{lm}(\Theta, \Phi), \quad (5)$$

with $(r_<, r_>)$ the (lesser, greater) of (r_α, r) and $\Theta_\alpha, \Phi_\alpha$ the angular coordinates of α . The attraction between the electrons and nucleus α in the HF approximation is

$$E_{n\alpha} = -\sum_{\mathbf{k}} N_{\mathbf{k}} \langle \psi_{\mathbf{k}} | V_\alpha | \psi_{\mathbf{k}} \rangle. \quad (6)$$

Each $\psi_{\mathbf{k}}$ is expanded in terms of the basis orbitals,

$$\psi_{\mathbf{k}} = \sum_{\mathbf{i}} C_{i\mathbf{k}} \Phi_{\mathbf{i}},$$

with $\Phi_{\mathbf{i}}$ given by (3). Then (6) can be expressed in terms of integrals of the form

$$\int_0^\infty dr g(r) \int_\pi^0 d\Phi \sin \Theta \int_0^{2\pi} d\Phi S_{l_i m_i}(\Theta, \Phi) S_{l_j m_j}(\Theta, \Phi) S_{lm}(\Theta, \Phi), \quad (7)$$

where $S_{l_i m_i}(\Theta, \Phi)$ and $S_{l_j m_j}(\Theta, \Phi)$ are from basis orbitals and $S_{lm}(\Theta, \Phi)$ from (5). The exact form of the radial integrands $g(r)$ is not important. The angular integral in (7) is zero unless²⁰

$$l_i + l_j > l \quad (8)$$

and

$$|l_i - l_j| < l.$$

Thus in an OCE basis, terms in (7) with l larger than twice the largest l -value in the basis vanish. If orbitals are included on another centre, their expansion in terms of spherical harmonics on the first centre is infinite; there would then be no largest l_i or l_j in (7). Thus a two-centre basis does not result in

neglect of higher l -terms in (5) so restricting the basis to a finite set on one centre causes truncation of the off-centre nuclear attraction energy⁴.

Similarly, the electron repulsion operator r_{12}^{-1} can be expanded

$$r_{12}^{-1} = 4\pi \sum_{l=0}^{\infty} \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} \sum_{m=-l}^l S_{lm}(\Theta_1, \Phi_1) S_{lm}(\Theta_2, \Phi_2),$$

with $(r_{<}, r_{>})$ now the (lesser, greater) of (r_1, r_2) . In evaluating $[pq | rs]$ terms arise containing the factors

$$\int_0^\pi d\Theta_1 \sin \Theta_1 \int_0^{2\pi} d\Phi_1 S_{l_p m_p}(\Theta_1, \Phi_1) S_{l_q m_q}(\Theta_1, \Phi_1) S_{lm}(\Theta_1, \Phi_1)$$

and

$$\int_0^\pi d\Theta_2 \sin \Theta_2 \int_0^{2\pi} d\Phi_2 S_{l_r m_r}(\Theta_2, \Phi_2) S_{l_s m_s}(\Theta_2, \Phi_2) S_{lm}(\Theta_2, \Phi_2);$$

the product of these vanishes unless $l_p + l_q > l$, and $l_r + l_s > l$, so there is also truncation of the electron repulsion energy in a finite OCE basis. In a given basis these errors can be reduced by adding orbitals of higher l .

3. CHOICE OF BASIS

The general form (3) of the STO contains the spherical harmonic $S_{lm}(\Theta, \Phi)$. Normalized associated Legendre polynomials are chosen as the Θ -dependent part²⁷. For the Φ -dependent factor there are two common choices: the complex functions $\exp(im\Phi)$ ²⁸, or the real functions $\sin|m|\Phi$ and $\cos|m|\Phi$ ^{27,29}. For this work the real functions were chosen because they lead to Fock matrices with real elements; with complex orbitals the Fock matrix is in general complex. Complex matrices have two disadvantages: they require twice as much computer memory as the corresponding real matrix, and many matrix diagonalization methods³⁰ are restricted to real matrices. Formulas for the real spherical harmonics are given in Reference 26.

For an SCF calculation of HCl the necessary m -values can be determined exactly. Consider HCl with Cl at the origin and the proton on the $+z$ -axis. The MO structure of HCl is³¹ $(1s\sigma)^2 (2s\sigma)^2 (2p\sigma)^2 (2p\pi)^4 (3p\pi)^4$. The σ MO's depend upon the angle Φ about the z -axis in the same way as the Φ -factor of a spherical harmonic with $m = 0$; the π MO's have the Φ -dependence of a spherical harmonic with $m = \pm 1$. Thus the Φ -dependence of all MO's of HCl is given correctly by a basis including STO's with only the three m -values $-1, 0$, and $+1$.

No limit can be placed on the n - or l -values needed. The n -value determines the sharpness of the radial peaking and the l -value the sharpness of the angular peaking. For $n > 1$, the radial factor of an STO,

$$R(n, \zeta, r) = r^{n-1} \exp(-\zeta r), \quad (9)$$

vanishes for $r = 0$ and approaches 0 as $r \rightarrow \infty$, with a maximum at a point r_{\max} between the extremes. The sharpness of this maximum is the width at half-height of (9). Differentiating (9):

$$r_{\max} = (n-1)/\zeta, \quad (\text{au}) \quad (10)$$

The widths at half height of the radial function (9) for values of n from 4 to 20 and $r_{\max} = 2.41$ au are compared with a similar value for the $1s$ orbital of H

TABLE I

Radial peaking of STO's. Widths at half height (au) for STO's with $r_{\max} = 2.41$ au

n	width (au)
4	3.32
5	2.87
6	2.56
7	2.33
8	2.15
9	2.00
10	1.90
11	1.80
12	1.72
13	1.64
14	1.57
15	1.52
16	1.47
17	1.42
18	1.37
19	1.34
20	1.30

(Table I), since orbitals are added to an OCE basis for HCl to approximate electron density *at the proton*. The radial part of the H 1s orbital is

$$R_{\text{H}}(r) = \exp(-r),$$

which falls to half its maximum value ($r_{\max} = 0$) at $r = 0.69$ au; the quantity corresponding to width at half height of the STO's on Cl is twice this, 1.38 au. This sharpness is attained for $n > 18$ (Table I). This peaking is illusory, occurring in all directions, though needed only at the proton³².

Orbitals with $n = 18$ are not used in OCE bases; in one approach³ n - and l -values are selected by constructing normalized OCE-MO's to maximize overlap with MO's from two-centre calculations; the exponents ζ are selected by minimizing the molecular energy in a series of calculations.

The present approach starts (in HCl) with an accurate published basis for Cl in a two-centre calculation of Cl_2 ³³ and adds orbitals to approximate the electron distribution near the proton. The basis enlargement process will be reported⁶. A rather small basis yields a lower molecular energy and several molecular properties closer to the HF limit for HCl than the 71-STO basis of Moccia⁸.

Moccia developed a large OCE basis for HCl by the first approach over a number of years^{3,8}. The basis includes 71 orbitals; only 51 are listed because each orbital with $m = 1$ there is another with identical n, l , and ζ but with $m = -1$. A similar convention is followed later in listing π MO's.

Orbitals 1 through 9 are essentially a triple- ζ set of 1s, 2s, and 3s orbitals (3 ζ -values for every, n, l, m combination). A 9s orbital with $r_{\max} = 2.34$ au (orbital 10) for electron density near the proton. The $p\sigma$ orbitals 11–17 follow a similar pattern, but with two $2p\sigma$ and four $3p\sigma$ orbitals included³⁴; the remaining σ -orbital pattern is less simple; for $1 < l < 3$ two orbitals of the

minimum $n (= l + 1)$ and at least one of a higher n for density at the proton are added. For $4 < l < 6$, there is one orbital with $n = l + 1$ and one with $n = 9$; for $l = 7$, the highest included, there is only the $n = 9$ orbital. The π orbitals follow a similar pattern with one less $l = 6$ orbital.

The π set is a radially flexible as the σ set; although there are 31 σ -orbitals and only 20 π -orbitals for each m -value, 10 of the σ -orbitals are s -orbitals ($l = 0$). For $l > 1$ there are 21 σ -orbitals and 20 π -orbitals, and the orbital of largest r_{\max} (orbital 44, $r_{\max} = 2.727$ au) is a π -orbital.

Two major criticisms can be made: first, it was too costly to energy-optimize the ζ of the whole 71-STO set; 43 orbitals were first selected and the energy minimized with respect to the ζ of these orbitals⁸; then several unimportant orbitals were discarded and orbitals with higher n and l added with exponents chosen to put r_{\max} near the proton. The exponents were not reoptimized after addition of these orbitals. Since several of the MO's involve the high- n basis orbitals heavily (Table V), the role of some orbitals of the 43-orbital set with low exponents (*i. e.* higher r_{\max}) is now taken by orbitals with higher n , and the charge distribution would be better approximated by increasing the exponents of some lower- n orbitals to give flexibility in the bonding region. Adjusting the orbital exponents would require much computer, time, so reoptimizing the 71-STO set was not undertaken.

Second, the large number of π orbitals. The bonding in HCl involves σ orbitals (in a minimal two-centre basis for HCl no π orbitals are included on H); it is better to leave the π basis at roughly the size for an accurate calculation on the Cl^- ion and make most of the orbital additions to the σ set. To avoid artificial deviations from spherical symmetry in MO's describing inner electron shells^{6,35} the exponents of, for example, the $2p$ π basis orbitals must equal those of the corresponding $2p$ σ set so that small polarization is produced by differences in the MO coefficients, when there is more than one $2p$ orbital of each symmetry. The basis in Table II, has differences of up to 0.1 between corresponding $2p$ σ and $2p$ π exponents. A calculation of Cl^- in this basis⁶ produced a charge distribution which deviated significantly from spherical symmetry.

The bases in this paper⁶ were constructed by adding orbitals with $n = 9$ and $r_{\max} = 2.4087$ au to the Gilbert-Wahl (GW) basis for Cl_2 ³³, which was developed from the basis for Cl of Bagus³⁶. The largest basis used (29 STO's) is given in Table III.

4. EVALUATION OF ELECTRONIC INTEGRALS

Techniques evaluating all the integrals which occur in an OCE-SCF calculation are well-known²⁸, except for the off-centre nuclear attraction integrals³⁷. The integral routines used were written independently and were designed to be completely general; there is no limit to the size of the n, l, m , or ζ parameters which the routines can handle except the largest number which the computer can represent.

It is important that one who writes routines for the evaluation of electronic integrals prove the accuracy of these routines, since the molecular energy and MO's are seriously affected if there are errors in integral evaluation³⁸. To this end derivations of the integral formulas are given²⁶ with comparisons between integrals evaluated by these routines and previously published values.

TABLE II

The Moccia⁸ OCE basis for HCl. 71 STO's, 31 σ orbitals and 20 π pairs

σ orbitals	n	l	m	ξ	r_{\max} (au)
1	1	0	0	23.980	0.000
2	1	0	0	15.305	0.000
3	1	0	0	10.000	0.000
4	2	0	0	8.502	0.118
5	2	0	0	6.297	0.159
6	2	0	0	4.000	0.250
7	3	0	0	1.767	1.132
8	3	0	0	1.104	1.812
9	3	0	0	0.805	2.484
10	9	0	0	3.419	2.340
11	2	1	0	8.885	0.113
12	2	1	0	5.725	0.175
13	3	1	0	4.361	0.459
14	3	1	0	2.004	0.998
15	3	1	0	1.222	1.637
16	3	1	0	0.862	2.320
17	9	1	0	3.419	2.340
18	3	2	0	2.224	0.899
19	3	2	0	1.492	1.340
20	6	2	0	2.137	2.340
21	9	2	0	3.419	2.340
22	4	3	0	1.675	1.791
23	4	3	0	2.125	1.412
24	9	3	0	3.419	2.340
25	5	4	0	2.000	2.000
26	9	4	0	3.419	2.340
27	6	5	0	2.000	2.341
28	9	5	0	3.419	2.340
29	7	6	0	2.564	2.340
30	9	6	0	3.419	2.340
31	9	7	0	3.419	2.340
π orbitals	n	l	m	ξ	r_{\max} (au)
32	2	1	1	8.990	0.111
33	2	1	1	5.720	0.175
34	3	1	1	4.330	0.462
35	3	1	1	2.340	0.855
36	3	1	1	1.270	1.575
37	6	1	1	2.137	2.340
38	9	1	1	3.419	2.340
39	3	2	1	1.700	1.176
40	3	2	1	1.100	1.818
41	4	2	1	1.200	1.667
42	7	2	1	2.564	2.340
43	4	3	1	1.600	1.875
44	4	3	1	1.100	2.727
45	7	3	1	2.564	2.340
46	5	4	1	1.500	2.667
47	9	4	1	3.419	2.340
48	6	5	1	2.136	2.341
49	9	5	1	3.419	2.340
50	8	6	1	2.990	2.341
51	9	7	1	3.419	2.340

TABLE III

GW + 9 OCE basis for HCl. 29 STO's, 19 σ orbitals, 5 π pairs. Basis developed from Cl_2 basis of Gilbert and Wahl³³

σ orbitals	n	l	m	ζ	r_{\max} (au)
1	1	0	0	18.424	0.000
2	2	0	0	16.187	0.062
3	2	0	0	6.092	0.164
4	3	0	0	2.608	0.767
5	3	0	0	1.597	1.252
6	2	1	0	10.267	0.097
7	2	1	0	5.608	0.178
8	3	1	0	2.608	0.767
9	3	1	0	1.463	1.367
10	3	2	0	1.943	1.029
11	9	0	0	3.32129	2.4087
12	9	1	0	3.32129	2.4087
13	9	2	0	3.32129	2.4087
14	9	3	0	3.32129	2.4087
15	9	4	0	3.32129	2.4087
16	9	5	0	3.32129	2.4087
17	9	6	0	3.32129	2.4087
18	9	7	0	3.32129	2.4087
19	9	8	0	3.32129	2.4087
20	2	1	0	10.267	0.097
21	2	1	1	5.608	0.178
22	3	1	1	2.608	0.767
23	3	1	1	1.463	1.367
24	3	2	1	1.943	1.029

5. ORGANIZATION OF THE SCF CALCULATION

The computer programme to perform the calculations will be published³⁹. Some general problems which arise in performing closed-shell SCF calculations will be discussed.

a) Orthonormalization of Basis

In Roothaan's⁴⁰

$$\mathbf{FC} = \mathbf{SCE}, \quad (11)$$

with \mathbf{F} the Fock matrix, \mathbf{C} the coefficient matrix of the MO's, \mathbf{S} the overlap matrix of the basis set, and \mathbf{E} , the diagonal eigenvalue matrix, each iteration of the SCF process involves one solution, finding \mathbf{C} and \mathbf{E} given \mathbf{F} and \mathbf{S} . If the $n \times n$ matrix \mathbf{A} has an inverse, (11) can be rewritten

$$\mathbf{FAA}^{-1}\mathbf{C} = \mathbf{SAA}^{-1}\mathbf{CE};$$

multiplying both sides on the left by \mathbf{A}^+ , the transpose or (if \mathbf{A} is complex) conjugate transpose of \mathbf{A} ,

$$(\mathbf{A}^+\mathbf{FA})(\mathbf{A}^{-1}\mathbf{C}) = (\mathbf{A}^+\mathbf{SA})(\mathbf{A}^{-1}\mathbf{C})\mathbf{E}. \quad (12)$$

Suppose \mathbf{A} has been chosen so that

$$\mathbf{A}^+\mathbf{SA} = \mathbf{I}, \quad (13)$$

with \mathbf{I} the $n \times n$ identity matrix. Then, defining $\mathbf{F}' = \mathbf{A}^+ \mathbf{F} \mathbf{A}$ and $\mathbf{C}' = \mathbf{A}^{-1} \mathbf{C}$, (12) becomes

$$\mathbf{F}' \mathbf{C}' = \mathbf{C}' \mathbf{E},$$

or

$$\mathbf{C}'^{-1} \mathbf{F}' \mathbf{C}' = \mathbf{E}. \quad (14)$$

Since \mathbf{F} is symmetric, \mathbf{C}' can be found such that \mathbf{E} is diagonal and real and \mathbf{C}' is unitary (i. e. $\mathbf{C}'^{-1} = \mathbf{C}'^+$)⁴¹. Efficient computer routines exist which find \mathbf{C}' and \mathbf{E} in (14)³⁰.

Thus the problem in solving (11) is finding \mathbf{A} such that (13) is satisfied, which is equivalent to transforming the given basis to an orthonormal set. The method used here is the Löwdin Orthogonalized Atomic Orbital (OAO) method^{42,43}, where

$$\mathbf{S}^{-\frac{1}{2}} = \mathbf{U} \mathbf{D}^{-\frac{1}{2}} \mathbf{U}^+, \quad (15)$$

with \mathbf{U} a unitary matrix satisfying

$$\mathbf{U}^+ \mathbf{S} \mathbf{U} = \mathbf{D}, \quad (16)$$

with \mathbf{D} diagonal. $\mathbf{D}^{-1/2}$ is a diagonal matrix whose non-zero elements are the reciprocal square roots of the corresponding elements of \mathbf{D} . Substituting on the left of (13),

$$\left(\mathbf{S}^{-\frac{1}{2}}\right)^+ \mathbf{S} \mathbf{S}^{-\frac{1}{2}} = \mathbf{U} \mathbf{D}^{-\frac{1}{2}} \mathbf{U}^+ \mathbf{S} \mathbf{U} \mathbf{D}^{-\frac{1}{2}} \mathbf{U}^+ = \mathbf{U} \mathbf{D}^{-\frac{1}{2}} \mathbf{D} \mathbf{D}^{-\frac{1}{2}} \mathbf{U}^+ = \mathbf{I},$$

so (13) is satisfied. The problem with this method is that if the basis is or is nearly linearly dependent, the diagonalization (16) gives an inaccurate matrix \mathbf{U} . Problems of this kind were not encountered in OCE-SCF work.

b) Initiation of the Iterative Process

Since the elements of the Fock matrix depend on the MO coefficients, these coefficients must be guessed to start the iterative process. The published MO coefficients of Moccia⁸ were used to initiate the 71-STO calculations; calculations in the GW basis³³ were initiated with the MO coefficients of the Cl⁻ ion in this basis, which itself was initiated by simple guesses of orbital occupancies in the ion. Calculations in the enlarged GW bases⁶ were initiated with the coefficient matrices of the previous member of the series.

c) Convergence Criterion for the Iterative Process

For an SCF calculation one can check changes in the electronic energy

$$E_{\text{elec}} = \frac{1}{2} \sum_i \sum_j P_{ij} (H_{ij} + F_{ij}), \quad (17)$$

with P_{ij} , H_{ij} , and F_{ij} elements of the first-order density, one-electron Hamiltonian, and Fock matrices respectively, for convergence. The first convergence criterion used was that the relative change in E_{elec} between the i -th and the $i+1$ -st iterations be less than 0.5×10^{-12} ; *i. e.* that

$$\Delta E_i/E_i \equiv |E_{i+1} - E_i|/E_i < 0.5 \times 10^{-12}.$$

This is equivalent to requiring 12 significant figures in the electronic energy.

Even when this criterion was satisfied, the eigenvalue and coefficients of the highest occupied MO still changed in the fifth figure. Storing a whole coefficient matrix from iteration to iteration is costly of computer memory, so the following procedure was used. The energy criterion of 0.5×10^{-12} was satisfied. Thereafter the relative change in the eigenvalue of the highest occupied MO was checked until it fell below 0.5×10^{-6} . Experience has shown that the MO coefficients are accurate to the same number of decimal places as the corresponding eigenvalue. The coefficients of the highest occupied MO tend to be the most mobile from iteration to iteration for the following reason: the successive iterated Fock matrices are perturbations of the final Fock matrix; the n -th eigenvector at any iteration can be estimated to first order from the corresponding converged eigenvector by Rayleigh-Schrödinger perturbation theory⁴⁴,

$$\psi'_n = \psi_n^0 + \sum_{m \neq n} \frac{F_{mn}^{(1)}}{E_n^0 - E_m^0} + \dots, \quad (18)$$

with ψ_n^0 the converged n -th eigenvector of F , and $F_{mn}^{(1)}$ the difference between F_{mn} at self-consistency and F_{mn} at a particular iteration. E_n^0 and E_m^0 are eigenvalues of the converged eigenvectors. For HCl the lowest eigenvalue is much lower than the next lowest, and successive eigenvalues of occupied orbitals occur increasingly densely^{12,13}; thus the occupied eigenvector with the highest eigenvalue has many small denominators in the summation in (18) and hence relatively large corrections to ψ_n^0 ; the eigenvector with the lowest eigenvalue, however, always has relatively large denominators, and relatively small corrections to its eigenvector.

The first-order density matrix \mathbf{P} , with elements

$$\mathbf{P}_{ij} = \sum N_k C_{ik} C_{jk}, \quad (19)$$

with the sum over the MO's ψ_k and N_k the occupation number of ψ_k , is intermediate in accuracy between the electronic energy and the coefficients. It was observed in comparing preliminary calculations using an energy convergence criterion of 0.5×10^{-9} with later ones using 0.5×10^{-12} that the 0.5×10^{-9} criterion gave about six significant figures in the density matrix. *Roughly*, if 9 figures in the energy give 6 in the density matrix, then 12 in the energy give 8 in the density matrix. This could be tested by using a still smaller energy criterion, but this was not done since it might exceed the accuracy

limits of the integral routines. We estimate that the largest density matrix elements (≈ 1) have 8 significant figures, and the rest are accurate to the same number of decimal places.

6. OCE-SCF CALCULATION OF HCl

The Moccia⁸ OCE-SCF MO's for HCl (Table II) are for $R = 2.424$ au ($R_e = 2.4087$ au⁴⁵); the MO coefficients are in Table IV. This calculation was repeated with the above programme at the same internuclear distance; the MO's obtained are in Table V.

TABLE IV

Moccia's OCE-SCF MO's for HCl⁸, $R = 2.424$ au. Basis orbital numbers refer to Table II

$$E_{\text{elec}} = -467.07130 \text{ au}, \quad E_{\text{tot}} = -460.05810 \text{ au}$$

σ MO coefficients

basis orb.	1 σ	2 σ	3 σ	4 σ	5 σ
1	.09166	.00189	-.00003	-.02578	.00897
2	1.07967	-.20587	.00098	.27135	-.09095
3	-.22474	-.22100	.00074	-.24859	.09151
4	.11990	.11237	.00017	.56940	-.19886
5	-.06529	.93843	-.00566	-1.18487	.38862
6	.01557	.11949	.00130	.57420	-.19952
7	-.02284	-.00770	.00050	1.02584	-.24753
8	-.00159	-.00508	-.00005	.17500	-.09601
9	.00073	.00233	.00000	-.10227	.06199
10	.00264	.00803	-.00012	-.32499	.20646
11	.00021	.00059	.31653	-.01056	-.04967
12	-.00022	.00249	.63172	-.01773	-.19011
13	.00011	.00082	.11804	-.00486	.08679
14	-.00004	.00017	-.02183	.12564	.54599
15	.00001	-.00024	-.02286	-.00885	.61500
16	.00004	.00007	.00622	.00370	-.17441
17	.00001	.00022	.02737	.05752	-.08456
18	.00004	.00423	.00371	-.00019	0.6836
19	.00001	-.00717	-.00580	.07935	0.5115
20	-.00002	.00332	.00260	-.05934	.02405
21	.00001	.00081	.00076	.07764	.13177
22	.00000	-.00006	.00018	-.04105	-.01571
23	.00000	.00024	.00070	.03780	.03370
24	.00000	.00001	-.00059	-.06759	.11942
25	.00000	.00020	.00023	-.00107	.01311
26	.00000	-.00011	-.00008	.04053	.09389
27	.00000	-.00004	-.00006	-.02374	-.03729
28	.00000	.00010	.00015	.04760	.08541
29	.00000	-.00004	-.00002	-.03322	.05715
30	.00000	.00007	.00008	.04877	.08771
31	.00000	.00002	.00004	.01113	.02175
Eigenvalue (au)	-104.85153	-10.57766	-8.03915	-1.12047	-.62171

π MO coefficients

basis orb.	1π	2π
32	.30703	-.07154
33	.64523	-.19524
34	.12233	.01423
35	-.05300	.67714
36	.06102	.43384
37	-.07671	.03839
38	.04082	-.06366
39	-.02731	.02735
40	.09636	-.08101
41	-.03615	.01925
42	-.01247	.01127
43	.00112	.02340
44	-.00010	-.00454
45	-.00099	.00311
46	-.00003	.00062
47	.00006	.00989
48	.00000	-.00070
49	.00003	.00694
50	.00001	.00382
51	.00001	.00234
Eigenvalue (au)	-8.03815	-.48078

The eigenvalues differ by about 0.007 au, with Moccia's lower; the electronic energies differ by about the same amount. In the higher energy MO's, such as 5σ and 2π , there are large differences in the coefficients (*e.g.* basis orbital 15 in 5σ , orbital 36 in 2π). The present integral routines were thoroughly tested; the source of differences is the *integral storage length*. A test calculation truncating our integrals to 6 significant figures⁴⁶ agreed well with the Moccia results.

Since the differences between the calculations produced important differences in the calculated EFG, further discussion of results in the 71-STO basis⁸ refers to calculations performed in this laboratory with integrals stored to 16 figures. Calculations in the basis series constructed from the GW Cl₂ basis³³ are also presented.

a) Calculations of HCl at Equilibrium Separation

Since the EFG at the Cl nucleus contains a nuclear contribution dependent on the internuclear distance, for comparison with experiment the OCE-SCF wavefunction must be calculated at the experimental equilibrium internuclear distance, 2.4087 au (corrections for vibrational motion will be discussed later⁴⁷). The OCE-SCF wavefunction in the 71-STO basis for $R = 2.4087$ au is presented in Table VI: and that in the GW+9 basis (largest of the GW series) of Table III in Table VII.

TABLE V

71-STO OCE-SCF MO's for HCl, $R = 2.424$ au, this work. Basis orbital numbers refer to Table II

$$E_{\text{elec}} = -467.06581 \text{ au}, \quad E_{\text{tot}} = -460.05261$$

σ MO coefficients

basis orb.	1 σ	2 σ	3 σ	4 σ	5 σ
1	.091670	.001782	-.000030	-.030236	.010533
2	1.079626	-.205252	.000910	.305130	-.103061
3	-.224687	-.221808	.000722	-.296716	.108246
4	.119841	.113155	.000170	.636724	-.223144
5	-.065240	.937814	-.005461	-1.258001	.417160
6	.015554	.119670	.001370	.608137	-.212826
7	-.002838	-.007751	.000493	1.054873	-.236498
8	-.001574	-.004874	-.000072	-.017368	-.023937
9	.000721	.002220	.000014	-.008657	.026224
10	.002628	.007966	-.000107	-.238332	.178162
11	.000204	.000537	.316378	-.010524	-.050023
12	-.000214	.002290	.631979	-.017689	-.187287
13	.000105	.000832	.117847	-.005791	.073906
14	-.000035	.000151	-.022316	.137986	.685915
15	-.000036	-.000226	-.020702	-.046728	.189244
16	.000011	.000066	.005376	.019222	.008768
17	.000039	.000219	.026378	.073757	.074352
18	.000015	.004340	.003376	-.007574	.062203
19	-.000019	-.007352	-.005226	.094545	.065196
20	.000013	.003489	.002400	.076911	.005896
21	-.000005	.000734	.000637	.086517	.141916
22	.000000	-.000086	.000146	-.042512	-.018086
23	-.000004	.000238	.000727	.038534	.034955
24	.000002	.000037	-.000575	.069397	.121588
25	-.000002	.000206	.000275	.000138	-.008866
26	.000001	-.000112	-.000116	.040025	.090390
27	.000001	-.000042	-.000058	-.025685	-.040732
28	-.000001	.000097	.000153	.049849	.089026
29	.000001	-.000057	-.000081	-.037179	-.064425
30	-.000001	.000092	.000142	.052879	.094983
31	.000000	.000019	.000039	.011335	.021975
Eigen- value (au)	-104.845293	-10.571650	-8.033174	-1.109650	-614132

π MO coefficients

basis orb.	1 π	2 π
32	.307736	-.073836
33	.643627	-.190227
34	.125505	-.005041
35	-.062738	.771225
36	.085110	.186711
37	-.103622	.171809
38	.049498	-.010326
39	.019308	.059578
40	-.065216	-.131750
41	.043036	.092976
42	.007474	.026113
43	.001155	.023257
44	-.000103	-.005019
45	-.001021	.003552
46	-.000026	.000685
47	.000060	.009799
48	-.000006	-.000930
49	.000029	.007160
50	.000015	.003831
51	.000010	.002349
Eigen- value (au)	-8.032160	-4.74829

b) Partitioning of the Electronic Energy

The electronic energy (17) can be partitioned

$$E_{\text{elec}} = E_k + E_n + E_r, \quad (20)$$

with E_k , E_n , and E_r representing kinetic, nuclear attraction, and electron repulsion energy. The first two terms can be directly partitioned into MO contributions,

$$E_k = \sum_j E_k^j, \quad E_k^j = -\frac{1}{2} N_j \langle \psi_j | \nabla^2 | \psi_j \rangle \quad (21)$$

and

$$E_n = \sum_j E_n^j, \quad E_n^j = -N_j \langle \psi_j | \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}} | \psi_j \rangle, \quad (22)$$

α ranging over nuclei and j over MO's. For closed shell molecules, the electron repulsion energy can be written⁴⁰,

$$E_r = \sum_l^{\text{occ}} \sum_m^{\text{occ}} (2J_{lm} - K_{lm}), \quad (23)$$

(23) can be partitioned,

$$E_r = \sum_l^{\text{occ}} E_r^l, \quad E_r^l = \sum_m^{\text{occ}} (2J_{lm} - K_{lm}). \quad (24)$$

TABLE VI

71-STO OCE-SCF MO's for HCl, R = 2.4087 au (equilibrium distance), this work.
Basis orbital numbers refer to Table II

$$E_{\text{elec}} = -467.110343555 \text{ au}, \quad E_{\text{tot}} = -460.052594562 \text{ au}$$

σ MO coefficients

basis orb.	1 σ	2 σ	3 σ	4 σ	5 σ
1	.091670	.001781	-.000032	-.030112	.010761
2	1.079625	-.205248	.000924	.304084	-.105032
3	-.224686	-.221809	.000701	-.295327	.110723
4	.119841	.113158	.000199	.634410	-.227399
5	-.065240	.937791	-.005490	-1.254730	.423567
6	.015554	.119689	.001382	.606324	-.216185
7	-.002838	-.007743	.000509	1.055546	-.263282
8	-.001574	-.004874	-.000068	-.019138	-.028528
9	.000721	.002220	-.000012	-.008023	.027585
10	.002628	.007961	-.000118	-.238212	.178306
11	.000203	.000537	.316378	-.010921	-.050463
12	-.000214	.002284	.631975	-.017860	-.186765
13	.000105	.000831	.117845	-.006335	.072664
14	-.000035	.000161	-.022299	.142439	.691212
15	-.000036	-.000221	-.020691	-.048699	.182983
16	.000011	.000064	.005373	.019741	.008618
17	.000039	.000211	.026363	.073848	.074437
18	.000015	.004311	.003356	-.009365	.058740
19	-.000019	-.007286	-.005162	.100752	.075486
20	.000013	.003459	.002374	-.081324	-.003198
21	-.000005	.000723	.000620	.087095	.142830
22	.000000	-.000084	.000149	-.044176	-.022354
23	-.000004	.000244	-.000739	.040367	.038526
24	.000002	.000031	-.000595	.069757	.122019
25	-.000002	.000215	.000296	.001294	-.006872
26	.000001	-.000121	-.000135	.039217	.088204
27	.000001	-.000042	-.000056	-.026198	-.041544
28	-.000001	.000097	.000152	.050529	.089604
29	-.000001	-.000057	-.000080	-.037890	-.065301
30	-.000001	.000092	.000141	.053697	.095705
31	.000000	.000020	.000039	.011423	.021891
Eigen- value (au)	-104.845043	-10.571612	-8.033157	-1.111257	-.615937

π MO coefficients

basis orb.	1π	2π
32	.307732	-.073810
33	.643622	-.190175
34	.125519	-.005163
35	-.062740	.771408
36	.085112	.186757
37	-.103625	.171217
38	.049499	-.009963
39	.019249	.059531
40	-.065004	-.130000
41	.042897	.091644
42	.007447	.025875
43	.001160	.023808
44	-.000104	-.005289
45	-.001024	.003289
46	-.000027	.000534
47	.000061	.009963
48	-.000006	-.001024
49	.000028	.007277
50	.000015	.003848
51	.000010	.002359
Eigen- value (au)	-8.032113	-.475190

Table VIII gives the partitioning of E_k , E_n , and E_r into MO contributions for the wavefunctions of Tables VI and VII. E_n is resolved into contributions from the proton and the Cl nucleus.

c) *Virial Theorem; Calculated R_e*

The exact wavefunction for HCl at R_e satisfies the virial theorem^{48,49}

$$E_{\text{pot}}/E_k = -2, \quad (25)$$

with E_{pot} the total potential energy and E_k the kinetic energy of the electrons, assuming stationary nuclei. At $R = 2.4087$ au, the 71-STO basis gave -2.000526 ; the GW + 9 basis gave -2.000126 . (25) holds for exact and HF wavefunctions for nuclei at the calculated equilibrium position. Although $R_e = 2.4087$ au for HCl experimentally, it is *not* the R_e calculated in the OCE bases, so the virial theorem is not expected to hold in these bases for $R = 2.4087$ au. To locate the OCE-SCF R_e values, calculations were done at $R = 2.3887, 2.3987, 2.4087, 2.4187, \text{ and } 2.4287$ au for the 71-STO basis and additionally at $R = 2.3787$ and 2.4387 au for the GW+9 basis⁴⁷; a polynomial was fitted⁵⁰ to the total energies and the OCE-SCF R_e calculated by differentiating and setting to zero. This gave $R_e = 2.4181$ au for the 71-STO basis and 2.5098 au for the GW + 9 basis, which indicates the more accurate R -dependence of the 71-STO wavefunction⁴⁷. Polynomial interpolation of virial ratios in the 71-STO basis gave a ratio of -2.00054 at $R = 2.4181$ au; no similar calculation was done for the GW+9 basis since the calculated R_e lay outside the range

TABLE VII

OCE-SCF MO's for HCL, $R = 2.4087$ au (the equilibrium distance), in the GW + 9 basis of Table III

$$E_{\text{elec}} = -467.126687373, \quad E_{\text{tot}} = -460.068938380$$

σ MO coefficients

basis orb.	1 σ	2 σ	3 σ	4 σ	5 σ
1	-.862215	.241176	.001031	-.068740	-.020113
2	-.164576	.140574	.000582	-.050338	-.015187
3	-.001581	-1.079872	-.004792	.376436	.112567
4	.000243	-.031849	.002367	-.771859	-.274708
5	-.000171	.025517	-.002162	-.385324	.018969
6	-.000117	-.000328	.205165	.005950	-.041974
7	.000070	-.003269	.821186	.028664	-.189712
8	-.000055	-.000961	.023040	-.050990	.423846
9	.000081	.000752	-.010288	-.105968	.521532
10	-.000007	-.000678	.000864	-.052502	.120225
11	.000069	-.011499	.001186	-.026842	.057587
12	-.000049	-.000511	.003157	-.025759	.084182
13	.000005	.000394	-.000322	-.057651	.160545
14	.000002	-.000159	.000209	-.062789	.138888
15	.000001	-.000098	.000167	-.040680	.084296
16	.000001	-.000063	.000114	-.026350	.053252
17	.000000	-.000042	.000078	-.017425	.034550
18	.000000	-.000028	.000054	-.011753	.022946
19	.000000	-.000017	.000037	-.008023	.015628
Eigen-value (au)	-104.846577	-10.571981	-8.041414	-1.115449	-6.21367

π MO coefficients

basis orb.	1 π	2 π
20	.206048	-.051177
21	.821462	-.228703
22	.018728	.540581
23	-.005187	.564570
24	.000235	.027335
Eigen-values (au)	-8.037564	-0.0476228

TABLE VIII

OCE-SCF energy partitioning, 71-STO and GW + 9 bases, $R = 2.4087$ au (equilibrium distance), this work. E_k , E_n , and E_r defined below equation (20)

A. 71-STO (wavefunction of Table VI). Energies in au.

MO	E_k	$E_{n,\text{tot}}$	$E_{n,\text{Cl}}$	$E_{n,\text{H}}$	E_r
1 σ	274.285943	-563.872979	-563.042652	-830326	39.948475
2 σ	43.560534	-113.479046	-112.648083	-830963	24.387644
3 σ	41.136374	-109.549221	-108.707555	-841666	26.173266
4 σ	5.599702	-29.245521	-28.218354	-1.027167	10.711652
5 σ	3.876404	-23.827384	-22.577841	-1.249543	9.359553
1 π	41.248925	-109.682513	-108.857984	-824529	26.184681
2 π	4.426839	-25.154384	-24.419729	-734655	9.888583
Totals	459.810485	-1109.647945	-1101.749911	-7.898033	182.727118

B. GW + 9 (wavefunction of Table VII). Energies in au.

MO	E_k	$E_{n,\text{tot}}$	$E_{n,\text{Cl}}$	$E_{n,\text{H}}$	E_r
1 σ	274.261578	-563.848572	-563.018246	-830326	39.946920
2 σ	43.421407	-113.311710	-112.480691	-831018	24.373170
3 σ	41.219572	-109.635223	-108.793710	-841513	26.166412
4 σ	5.712308	-29.392261	-28.375288	-1.016973	10.724528
5 σ	3.856888	-23.663926	-22.418303	-1.245623	9.282152
1 π	41.327918	-109.766012	-108.941503	-824509	26.181483
2 π	4.441651	-25.215903	-24.488405	-727498	9.910898
Totals	460.010891	-1109.815522	-1101.946054	-7.869467	182.677944

of calculations. The deviation of these ratios from -2 measures the limitations of the OCE bases; a near HF two-centre calculation of HCl at $R = 2.4087$ au gives the ratio -2.0003^{13} .

d) Cusp Conditions

Since the HF equation for each orbital has the same singularities as the total Hamiltonian, each HF orbital ψ_i must (if $\psi_i(r_{i\alpha} = 0) \neq 0$) satisfy (2). The case $\psi_i(r_{i\alpha} = 0) = 0$, which arises for π MO's, was treated by Pack and Brown⁵¹. Any MO can be expanded about nucleus α ,

$$\psi = \sum_{l=0}^{\infty} \sum_{m=-l}^l r^l f_{lm}(r_{\alpha}) S_{lm}(\Theta_{\alpha}, \Phi_{\alpha}); \quad (26)$$

the exact form of the $f_{lm}(r_{\alpha})$ is not important. Pack and Brown showed that for H ψ to remain finite at $r_{\alpha} = 0$, the relation

TABLE IX

Test of cusp condition, OCE-SCF MO's for HCl, $R = 2.4087$ au (equilibrium distance), GW + 9 and 71-STO bases, this work.

A. 71-STO (wavefunction of Table VI)

MO	$f_{\bar{l}m}(0)^a$	$df_{\bar{l}m}(r)/(dr)_{r=0}^a$	cusp ratio ^b
1 σ	-38.53566	657.46495	-17.06121
2 σ	10.77286	-182.27271	-16.91962
3 σ	-.04162	.70227	-16.87197
4 σ	-3.00834	47.48094	-15.78311
5 σ	.85974	-13.31622	-15.48871
1 π	144.26299	-2196.50257	-15.22568
2 π	-37.83658	580.29930	-15.33699

B. GW + 9 (wavefunction of Table VII)

MO	$f_{\bar{l}m}(0)^a$	$df_{\bar{l}m}(r)/(dr)_{r=0}^a$	cusp ratio ^b
1 σ	-38.46951	652.20231	-16.95375
2 σ	10.76057	-182.20243	-16.93242
3 σ	.04598	-.79021	-17.18585
4 σ	-3.06696	50.45245	-16.45030
5 σ	-.89737	14.67686	-16.35545
1 π	151.00611	-2442.06206	-16.17192
2 π	-39.62862	645.33162	-16.28432

^a Defined in equation (27) of text. For σ MO's, $\bar{l} = 0$; for π MO's, $\bar{l} = 1$.

^b For exact Hartree-Fock orbitals, the cusp ratio = -17.

$$(\bar{l} + 1) (df_{\bar{l}m}(r_\alpha)/dr_\alpha)_{r_\alpha=0} = -Z_\alpha f_{\bar{l}m}(0)$$

must hold, where \bar{l} is the lowest l in (26) for which $f_{\bar{l}m}(0) \neq 0$. The ratio of the left side to $f_{\bar{l}m}(0)$ is called the cusp ratio here, although the term is strictly correct only if $\psi(r_\alpha = 0) \neq 0$. For OCE-SCF MO's if α is the expansion centre the $f_{\bar{l}m}(r)$ are linear combinations of radial portions (9) of STO's. Cusp ratios for the occupied MO's of HCl in the 71-STO and GW+9 bases at $R = 2.4087$ au are presented in Table IX. Note that the cusp ratios of higher energy MO's (all cusp ratios = -17 for the HF orbitals) deteriorate in the 71-STO basis, but that fair accuracy is retained in the GW+9 basis.

e) Dipole Moment

For HCl with the proton on the +z-axis, the electronic contribution to the dipole moment μ is

$$\mu_{\text{elec}} = -\sum_{\mathbf{k}} N_{\mathbf{k}} \langle \psi_{\mathbf{k}} | z | \psi_{\mathbf{k}} \rangle,$$

TABLE X

OCE-SCF dipole moments, 71-STO and GW + 9 wavefunctions for HCl, R = 2.4087 au (equilibrium distance), this work

MO	μ_{elec} (au)	
	71-STO (Table VI)	GW+9 (Table VII)
1 σ	-.000016	-.000017
2 σ	-.003564	-.003956
3 σ	.002420	.002988
4 σ	-.772231	-.784781
5 σ	-.838568	-.910279
1 π	-.000335	-.000076
2 π	.135995	-.088381
Total (au)	-1.884619	-1.872958
Total (D)	-4.789910	-4.760273
μ_{nuc} (au)	2.408700	2.408700
μ_{nuc} (D)	6.121904	6.121904
μ_{tot} (au)	.524081	.535742
μ_{tot} (D)	1.331994	1.361631

Experimental⁵² $\mu_{\text{tot}} = 1.1085$ D.

with the sum over MO's. Table X gives the MO analysis of μ_{elec} for the GW+9 and 71-STO OCE-SCF calculations at $R_e = 2.4087$ au, as well as μ_{elec} in debyes (D) and au. The total dipole moment is also listed,

$$\mu = \mu_{\text{elec}} + \mu_{\text{nuc}}$$

The nuclear contribution is the proton charge times its distance from the Cl nucleus. The conversion factor $1 \text{ au} = 2.45158\text{D}^{13}$ was used. The 71-STO and GW+9 contributions to μ_{elec} are similar, the result in the 71-STO basis being slightly closer to the experimental value (1.1085D^{52}). Both OCE bases underestimate the magnitude of μ_{elec} , because they place too little electron density near the proton. This is expected, since STO's centered on Cl are unable to produce a sharp peak in the electron density at the proton. The OCE calculated μ 's differ from experiment by about 20%.

f) Molecular Quadrupole Moment

The molecular quadrupole moment in au is defined by

$$\Theta = \sum_{\alpha} Z_{\alpha} r_{\alpha}^2 - \frac{3}{2} \langle z^2 \rangle + \frac{1}{2} \langle r^2 \rangle; \quad (28)$$

$\langle z^2 \rangle$ and $\langle r^2 \rangle$ are expectation values of the indicated one-electron operators (28) transforms under a change of origin,

$$\Theta' = \Theta - 2\mu\Delta,$$

with μ defined above and Δ the distance of the origin shift along the molecular axis¹³ For comparison with experiment, the origin must coincide with the molecular centre of mass, which lies 0.06753 au from the Cl nucleus¹³. On the basis of several experimental measurements, the recommended experimental value⁵³ for Θ of HCl is 3.8×10^{-26} esu-cm². At $R = 2.4087$ au the 71-STO basis gives 3.95×10^{-26} esu-cm², the GW + 9 3.80×10^{-26} . Both agree well with experiment, the GW+9 particularly well, even though $\langle z^2 \rangle$ and $\langle r^2 \rangle$ depend strongly on regions of space far from the Cl nucleus. However Θ is a measure of the deviation of the charge distribution from spherical symmetry; it is shown later⁴⁷ that the GW+9 basis reproduces these deviations extremely well. Calculations of Θ in the two bases are summarized in Table XI.

TABLE XI

Molecular quadrupole moment and related quantities, 71-STO and GW + 9 OCE-SCF wavefunctions, $R = 2.4087$ au (equilibrium distance), this work

MO	$\langle z^2 \rangle$ (au)		$\langle r^2 \rangle$ (au)	
	71-STO ^a	GW+9 ^b	71-STO ^a	GW+9 ^b
1 σ	.007467	.007468	.022400	.022405
2 σ	.154533	.154452	.462924	.462971
3 σ	.246423	.245301	.410569	.408328
4 σ	2.744387	2.831999	6.253550	6.348369
5 σ	6.361377	6.695791	9.378785	9.754053
1 π	.081895	0.81425	.409296	.407124
2 π	1.798804	1.663878	8.425603	8.313055
Total	13.275585	13.425616	34.198027	34.436985

$$\frac{1}{2} (3 \langle z^2 \rangle - \langle r^2 \rangle)_{\text{elec}} = 2.814364 \text{ au (71-STO)}$$

$$= 2.919932 \text{ au (GW + 9)}$$

$$\frac{1}{2} (3 \langle z^2 \rangle - \langle r^2 \rangle)_{\text{nuc}}^c = 5.801836 \text{ au}$$

$$\text{Molecular quadrupole moment (esu-cm}^2\text{)}^d = 3.9471 \times 10^{-26} \text{ (71-STO)}$$

$$= 3.7966 \times 10^{-26} \text{ (GW + 9)}$$

Recommended experimental value⁵³: 3.8×10^{-26} esu-cm²

^a Table VI.

^b Table VII.

^c Contribution from a proton 2.4087 au from the coordinate center on the $+z$ -axis.

^d In molecular center-of-mass coordinates. Conversion factor is $1 \text{ au} = 1.3449 \times 10^{-26}$ esu-cm². Experimental dipole moment⁵².

g) Electrostatic Force on the Cl Nucleus

At the equilibrium internuclear distance there is no net force on either nucleus in HCl. Since the experimental R_e does not coincide with the OCE-SCF

TABLE XII

Hellman-Feynman force on the Cl nucleus, 71-STO and GW + 9 OCE-SCF wavefunctions, R = 2.4087 au (equilibrium distance), this work

MO	$\langle z/r^3 \rangle$ (au)	
	71-STO ^a	GW+9 ^b
1σ	.014937	.015939
2σ	.024491	.027064
3σ	-.018271	.151849
4σ	.152157	-.020608
5σ	-.063156	-.054857
1π	.002362	.000280
2π	.017936	.018085
Total	.150754	.156117

$$\langle z/r^3 \rangle_{\text{nuc}}^c = .172359$$

Hellman-Feynman force on Cl^d = -.367289 au (71-STO)

= -.276114 au (GW + 9)

^a Table VI.

^b Table VII.

^c Due to proton 2.4087 au from coordinate center on +z-axis.

^d Equal to $-17 (\langle z/r^3 \rangle_{\text{nuc}} - \langle z/r^3 \rangle_{\text{elec}})$ The Hellmann-Feynman force for the exact wavefunction is zero.

TABLE XIII

$\langle r^{-1} \rangle$ and $\langle r^{-2} \rangle$ 71-STO and GW + 9 OCE-SCF wavefunctions, R = 2.4087 au (equilibrium distance) this work. No experimental values available

MO	$\langle r^{-1} \rangle$ (au)		$\langle r^{-2} \rangle$ (au)	
	71-STO ^a	GW+9 ^b	71-STO ^a	GW+9 ^b
1σ	33.120156	33.118720	1106.373872	1105.520522
2σ	6.626358	6.616511	90.299100	90.060466
3σ	6.394562	6.399630	28.327213	28.508806
4σ	1.659903	1.669135	7.850022	8.050258
5σ	1.328108	1.318724	2.323223	2.354455
1π	6.403411	6.408324	28.414347	28.577817
2π	1.436455	1.440494	2.286048	2.300540
Total	64.808818	64.820356	1296.574218	1296.251221

^a Table VI.

^b Table VII.

TABLE XIV

Comparison of properties calculated from the 71-STO and GW + 9 OCE-SCF wavefunctions for HCl with the two-center results of McLean and Yoshimine¹³ and Cade and Huo¹². All wavefunctions for R = 2.4087 au (equilibrium distance). Except as noted, all two-center properties from the compilation of McLean and Yoshimine¹³

Property	McL-Yosh ¹³	Cade-Huo ⁵⁶	GW + 9 ^b	71-STO ^a
Electronic energy (au)	-467.1696	-467.1680	-467.1267	-467.1103
Total energy (au)	-460.1119	-460.1103	-460.0689	-460.0526
Potential energy (au)	-920.2110	-920.2049	-920.0798	-919.8631
Kinetic energy (au)	460.0991	460.0946	460.0109	459.8105
Virial ratio ($E_{\text{pot}}/E_{\text{kin}}$)	-2.00003	-2.00003	-2.00013	-2.00053
Orbital eigenvalues (au)				
1 σ	-104.8479	-104.8485	-104.8466	-104.8450
2 σ	-10.5732	-10.5741	-10.5720	10.5716
3 σ	-8.0405	-8.0420	-8.0414	-8.0332
4 σ	-1.1164	-1.1168	-1.1154	-1.1113
5 σ	-.6254	-.6262	-.6214	-.6159
1 π	-8.0387	-8.0394	-8.0376	-8.0321
2 π	-.4763	-.4762	-.4762	-.4752
$\langle r^{-1} \rangle^c$ (au)	64.8218	64.8209	64.8204	64.8088
$\langle r^2 \rangle^c$ (au)	34.2597	34.2639	34.4370	34.1980
$\langle z \rangle^c$ (au)	1.9307	1.9379 ⁴⁷	1.8730	1.8846
$\langle z^2 \rangle^c$ (au)	13.3887	13.3622	13.4256	13.2756
Dipole moment (D)	1.215	1.197 ⁴⁷	1.362	1.332
Molecular quadrupole moment ($\times 10^{-26}$ esu-cm ²)	3.74	3.80	3.80	3.95
Force on Cl nucleus (Hellman-Feynman (au))	-.0682	-.1821	-.2761	-.3673

^a Table VI.

^b Table VII.

^c Measured from Cl nucleus.

calculated R_e , the OCE-SCF wavefunctions at the experimental R_e give a non-zero force on both nuclei. The difference of this quantity from zero indicates the deviation of the approximate wavefunction from the exact wavefunction, for which forces on the nuclei are equal to the average electrostatic forces (Hellman-Feynman theorem⁵⁴); the operator for the electrostatic force in the z-direction on nucleus α is $Z_\alpha (z_\alpha/r_\alpha^3)$, with Z_α the atomic number and z_α the distance along the z-axis from nucleus α . Calculations of this quantity with α the Cl nucleus for the OCE-SCF wavefunctions in the 71-STO and GW+9 bases are summarized in Table XII. The GW+9 basis gives a smaller force than the 71-STO basis although the 71-STO calculated R_e is much closer to the experimental value than that in the GW+9 basis. This illustrates the

approximate nature of the Hellman-Feynman theorem when applied to approximate wavefunctions⁵⁴.

h) Expectation Values of r^{-1} and r^{-2}

Expectation values of these operators are given in Table XIII. $\langle r^{-1} \rangle$ is compared with values from near HF two-centre calculations in the next section. No comparison is available for $\langle r^{-2} \rangle$. Note that for $\langle r^{-1} \rangle$ the 71-STO and GW+9 values are identical through the third figure, and for $\langle r^{-2} \rangle$ through the fourth.

7. COMPARISON WITH EXTENSIVE TWO-CENTRE AB-INITIO CALCULATIONS OF HCl

There are two near-HF two-centre SCF (TCE-SCF) calculations of HCl at $R = 2.4087$ au: one by Cade and Huo¹² in a 32-STO basis, and one by McLean and Yoshimine⁵⁵ in a 49-STO basis. McLean and Yoshimine¹³ published a number of one-electron properties calculated from both these wavefunctions; a number are compared with the corresponding quantities in the 71-STO and GW+9 bases in Table XIV. It is with these TCE-SCF properties that the OCE-SCF values should be compared for judging the suitability of the basis, since these TCE-SCF wavefunctions approximate closely the best possible single-determinant molecular wavefunction. Note that for expectation values of properties depending on regions far from the Cl nucleus (e.g. $\langle z^2 \rangle$, $\langle r^2 \rangle$), the 71-STO basis is closer to the TCE-SCF results; for those dependent on regions closer to the Cl nucleus (e.g. $\langle r^{-1} \rangle$, $\langle z/r^3 \rangle$), the GW+9 basis gives better agreement. Reasons for this are examined in the next paper.

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SAŽETAK

SCF računi jednog centra na klorovodiku. I. Dio

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Korištenjem dvaju različitih skupova osnovnih funkcija izvršeni su *ab initio* SCF računi jednog centra na klorovodiku. Valjanost dobivenih molekularnih orbitala provjerena je pomoću virijalnog teorema, uvjeta vrška i Hellman-Feynmanovog teorema. Izračunana svojstva ove molekule (dipolni moment, kvadrupolni moment i srednje vrijednosti za operatore r^{-1} i r^{-2}) za oba skupa osnovnih funkcija dobro se slažu s postojećim eksperimentalnim vrijednostima i rezultatima masivnih proračuna *ab initio* koji se nalaze blizu Hartree-Fockove granice.

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Prispjelo 12. ožujka 1976.