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One-Centre-Expansion Self-Consistent-Field Calculations on HCl. Part 2

Analysis of the Electric Field Gradient, EFG, at the Cl Nucleus from OCE-SCF Wavefunctions

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The 29-orbital one-centre-expansion self-consistent-field, OCE-SCF, basis for HCl[1] which gave a lower energy than a 71-orbital basis,[2] was used to calculate the electric field gradient, EFG, at the Cl atom in HCl and in Cl^-. The 29-orbital basis set[1] gave an electronic EFG of 3.4942 au, compared to the experimental value[3] of 3.4908 au. Calculations on Cl^- showed that the 71-orbital basis was badly chosen for the second electron shell. The effect of the basis on the 4σ and 5σ MO's is discussed, and the q_{elec} is analysed by orbital-pair type.

INTRODUCTION

The definition of the EFG runs counter to normal terminology in three ways: the gradient is a tensor rather than a vector, it refers to the negative of the electric field rather than the electric field itself, and its trace is zero and not $-4\pi\varrho$ as expected from Poisson's equations.

The evaluation of q_{zz} integrals in the OCE basis gives the traceless EFG automatically. The integrals are easily evaluated if Φ_i and Φ_j are centred on the point at which the EFG is evaluated; if $n_i = n_j = 1$ the integral is zero; otherwise it is a product of integrals. The tensor from these matrix elements and a molecular wavefunction will be traceless.

EVALUATION OF q_{zz} FROM AN OCE-SCF WAVEFUNCTION

q_{zz} will be written as q. The total molecular q due to the electrons is[1] negative,

$$q_{elec} = -\sum_k N_k < \Psi_k \,|\, \partial^2 V/\partial z^2 \,|\, \Psi_k > - \sum_k N_k \sum_i \sum_j C_{ik} C_{jk} < \Phi_i \,|\, \partial^2 V/\partial z^2 \,|\, \Phi_j > \quad (1)$$

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with N_k the occupation number of the MO $\Psi_{k'}$ and C_{ik} the coefficient of basis orbital Φ_i in Ψ_k: k is the MO, i and j are the basis orbitals. For the OCE-SCF calculation of HCl at $r = 2.4087$ au in the 71-orbital Moccia basis[1,2], the individual MO, and the total, q_{elec} by (1) are given in Table I. Comparison with the experimental value,[3] shows

$$q_{tot} = q_{elec} + q_{nuc} \tag{2}$$

6.5$^0/_0$ too high. The nuclear contribution, q_{nuc}, is

$$q_{nuc} = Z_\alpha (3 \cos^2 \Theta_\alpha - 1)/r_\alpha^{\,3} = 2/(2.4087)^3 \tag{3}$$

The largest density matrix elements D_{ij},

$$D_{ij} = \sum_k N_k C_{ik} C_{jk} \tag{4}$$

from the 71-orbital OCE-SCF calculation are accurate to 8 significant figures[1], as are the largest MO q_{elec}'s. The largest MO q_{elec} is the 3σ MO, at -160 au; an absolute uncertainty of $\pm 0.5 \times 10^{-5}$ au. Because there are 9 occupied MOs, the total q_{elec} is accurate to four decimal places.

TABLE I

The q *for MO's from OCE-SCF Calculations on HCl at* r = 2.4087 au *with Moccia and Modified Gilbert-Wahl Bases, for Comparison of* 3σ *and* 1πq

Aggrement is not expected for the 4σ, 5σ and 2π q since only the 3d orbital of the modified GW basis has r_{max} near the proton

M.O.[a]	Moccia basis[b]	Modified GW basis[c]	GW basis with Moccia 2pσ
1σ	−0.00010	−0.00001	−0.00001
2σ	−0.01230	−0.01752	−0.01742
3σ	−156.23061	−159.73185	−156.36762
4σ	−0.21301	−0.34254	−0.33411
5σ	−6.92658	−7.89900	−7.77587
1π	78.56465	80.10303	80.08024
2π	4.99300	4.99912	5.00292
total q_{elec}	3.73268	2.21339	5.67131
q_{tot}	3.87579	2.35650	5.81442

Experimental[3] $q_{elec} = 3.4908$ au
$q_{tot} = 3.6339$ au
and
$q_{nucl} = 2/(2.4087)^3 = 0.14311$ au.

[a] Accurate to 4 decimal places.

[b] Reference 2.

[c] Reference 1. The ζ of orbitals 10 and 15, the 3d orbitals, are reduced to 0.83032.

ANALYSIS BY MOs OF THE EFG; COMPARISON WITH THE Cl⁻ ION

The 1σ, 2σ, 3σ, 1π, 4σ, 5σ, and 2π orbitals of HCl correspond to the 1s, 2s, $2p_z$, $2p_x$ and $2p_y$, 3s, $3p_z$ and $3p_x$ and $3p_y$ orbitals of the Cl^- ion. The 1s, 2s, and three 2p orbitals do not bond the proton in HCl, consequently the 1σ, 2σ, 3σ and 1π MOs of the HCl are unchanged from the orbitals of the Cl^- ion. The EFG will show how true this is for a given wavefunction. The q for a spherical charge distribution is zero, therefore a closed, fully occupied, shell or subshell of electrons gives the q of the 1σ and 2σ orbitals, and the sum of the q's of the 3σ and two 1π orbitals, is zero, *if* these orbitals correspond exactly to the ionic orbitals. The total q of the 1σ MO of the 71-orbital wavefunction for HCl the sum of the q's of the 2σ, 3σ, and the two 1π MOs are listed in Table II.

TABLE II

Electron Shell Analysis of q_{elec} *for HCl and Cl⁻ in Several OCE Basis Sets*

Basis	Shell Contribution to q_{elec}/au		
	1	2	3
HCl			
Moccia 71-orbital[2]	—0.00010	0.88639	2.84640
Modified GW[a]	—0.00010	0.45669	1.75670
Cl⁻			
Moccia 71-orbital[2]	0.00000	0.46814	0.27836
Bagus[6] Clementi[5] GW[b]	0.00000	0.00000	0.00000

[a] Basis as in ref 7 but with orbitals 10 and 15 having exponent decreased to $\zeta = 0.83032$.
[b] Basis as in ref 7 but d-orbitals are excluded from occupied orbitals in Cl⁻ by symmetry.

The second shell q for HCl is not zero but nearly 25% of the total q_{elec}. Thus the Moccia 71-orbital basis is poor in the region of the second shell electrons, and the same defect appears when it is used in a calculation of the Cl⁻ ion.[2] The 71-orbital basis does not include σ and π basis orbitals in *equal numbers* or with *equal exponents*,[1,4] and it is not possible to construct a σ ionic orbital exactly degenerate with a π orbital pair. The q's for these Cl⁻ orbitals are given in Table III.

Two accurate, near Hartree-Fock limit wavefunctions for the Cl⁻ are expressed in STOs: Clementi's 25-orbital basis,[5] and Bagus's 28-orbital basis,[6] which has an energy closer to the Hartree-Fock limit. The q's for the orbitals of Cl⁻ were calculated from the published coefficients (the Clementi calculation was repeated in this laboratory; the coefficients agreed exactly with the literature values) and are listed in Table III, the analysis by electron shell is given in Table II. Serious disagreement between the 71-orbital Cl⁻ and the near Hartree-Fock Cl⁻ wave-functions occurs in the 2p orbitals: the 71-orbital basis gives q's of —156.5 au for the $2p_z$ and 78.5 au for the $2p_x$ and $2p_y$ orbitals, while the near Hartree-Fock functions[5,6] give q's of —160.7 au for $2p_z$ and 80.4 au for $2p_x$ and $2p_y$.

A series of small basis set calculations was done on HCl. The carefully optimized basis set of Gilbert and Wahl[7] for Cl_2, was chosen because of its small size (20 orbitals); experience had shown that it was as effective for investigating changes in the basis set of OCE-SCF wavefunctions of HCl as the 5-orbital larger Clementi Cl⁻ basis. The basis was modified: while the s and p orbitals are essentially atomic, the 3d orbital is a polarization and bonding

TABLE III

q_{elec} *by Orbitals for* Cl^-*, Several Basis Sets.*
All Values in au

Orbital (corresp. to HCl)	71-orbital[2]	Clementi[5]	Bagus[6]	GW[7]	GW-Bagus[a]
1s (1σ)	0.00000	0.0000	0.00000	0.00000	0.00000
2s (2σ)	— 0.00061	0.00000	0.00000	0.00000	0.00000
$2p_z$ (3σ)	— 156.54762	— 160.71315	— 160.72161	— 160.19510	— 155.41731
3s (4σ)	— 0.00008	0.00000	0.00000	0.00000	— 0.00005
$3p_z$ (5σ)	— 7.61509	— 9.19287	— 9.17898	— 9.14711	— 9.36622
$2p_x$, $2p_y$ (1π)	78.50819	80.35658	80.36081	80.09755	80.09464
$3p_x$, $3p_y$ (2π)	4.49258	4.59643	4.58949	4.57355	4.58016
Total q_{elec}	0.74650	0.00000	0.00000	0.00000	4.56602

[a]

GW — Bagus

orb	ζ	coeff
§ $2p_z$	7.535	— 0.842174
§ $2p_z$	4.385	0.167440
§ $4p_z$	7.200	— 0.370138
$3p_z$	2.608	— 0.75149
$3p_z$	1.463	0.027146
$3d_{z^2-r^2}$	1.943	0.000000

§ are the orbitals of the GW[7] basis replaced by orbitals of the Bagus basis[6].

function, whose optimal exponent is very dependent on the molecule considered;[7] the 3d orbital exponent was chosen[1] as $\zeta = 0.83032$ to give $r_{\max} = 2.4087$ au, so that its radial maximum coincided with the proton at the experimental equilibrium distance.

HCl was calculated with the GW basis[7] and a 3d exponent ζ of 0.83032. The $2p_z$ orbitals of the GW basis were replaced by the three orbitals from the 71-orbital Moccia basis[1,2] making large contributions to the $2p_z$ orbital of Cl^-; a $2p_z$ orbital with $\zeta = 5.725$, and a $3p_z$ orbital with exponent 4.361, and HCl was recalculated. Two points emerge: the q of the 3σ MO from the GW basis was —159.7 au, while q from the 3σ MO in the 21 orbital replacement basis was —156.4 au (Table I), and the total energy of the molecule in the GW basis is —459.914 au, and in the 21 orbital basis, —459.907 au. This difference is important because the energy is accurate to 12 significant figures. This is the same behaviour as observed in the 71 orbital calculations of HCl and Cl^- (Tables I and IV), and is induced in the GW basis by replacing the GW $2p\sigma$ set by the Moccia $2p\sigma$ set; the basis set is one orbital larger, gives a higher total energy so that the wavefunction is further from the Hartree-Fock limit than the 20 orbital basis wavefunction.

The inclusion of three appropriate σ orbitals from the Bagus basis gave the q from the $2p_z$ orbital even lower than from the Moccia basis, and far from the Hartree-Fock value (Table III). Thus while the Bagus basis produces a q of —160.7 au for the $2p_z$ orbital of Cl^-, and while only the three § orbitals of the basis contribute heavily to this ionic orbital, the insertion of these orbitals in the GW basis gives a q of —155.4 au for the $2p_z$ orbital. Thus replacing the orbitals of the Moccia basis, which contribute to the 3σ and 1π MOs, by the corresponding orbitals in the Bagus basis *cannot* improve the quality of these orbitals.

The Moccia 71-orbitals basis is not flexible in the second shell region; and this cannot be corrected by changing a few orbital exponents. A rebuilding of the basis would be necessary, preferably using the Bagus Cl^- basis as a starting point. This is prohibitively expensive, therefore further investigations of basis set effects were made using the GW basis, to obtain a basis with an energy lower than the Moccia 71-orbital basis, and with a q closer to experiment.[8]

THE 4σ AND 5σ MOs: BASIS SET EFFECTS

The important MO's determining q_{elec}, correspond to the third electron shell of HCl, the 4σ, 5σ, and 2π orbitals (Table II, Column 3). The $3p_x$ and $3p_y$ orbitals are unchanged from their form in Cl^-, therefore the important effects upon increasing the Cl^- basis will be in the 4σ and 5σ orbitals, and only σ orbitals have to be added to the basis, as confirmed by the q of the 2π MO in Table I and Table III for HCl and Cl^-.

To the GW basis, 9s, 9p, 9d, etc., orbitals with $m = 0$, $\zeta = 3.32129$ and $r_{max} = 2.4087$ au, the radial maxima at the proton, were successively added. The 3d exponent was that of the Gilbert-Wahl[7] calculation on Cl_2. The density near the proton is given by the $n = 9$ orbitals, while the 3d exponent has its molecular calculation value to give flexibility between the Cl nucleus and the proton.

The total and individual MO q_{elec} values for the expanded bases are given in Table IV. The addition stopped at the 9k (*1 — 8*) orbital, the largest allowed value of l; enlargement with higher n and higher l, would follow the same trends. The total q_{elec} for the basis through the 9k orbital (3.49418 au) closely agrees with Kaiser's[3] experimental value (3.4908 au).[8] The agreement is illusory*; addition of higher l-values raises q_{elec} above 3.5 au converging to roughly 3.6 au.

The greatest change in MO q_{elec} upon addition of higher l orbitals with $r_{max} = 2.4087$ au occurs in the 4σ (—0.28 au to —0.22 au) and 5σ (—8.20 au to —7.05 au) MOs. The 3σ MO changes about the same amount as the q_{elec} of the 4σ (—159.83 au to —159.75 au), but this change is much smaller relative to the q_{elec} of the MO. The 4σ and 5σ MO change, to lower absolute values of q_{elec}, corresponds to electron density transfer from the Cl nucleus (where $1/r^3$ is large) as expected for addition of basis orbitals with r_{max} far from the Cl nucleus.

Addition of orbitals of higher angular momentum quantum number allows a greater angular concentration of charge, because the interval between nodes of the Θ-dependent factor of the $m = 0$ spherical harmonic decreases[9] with increasing l. Since the proton is placed at $\Theta = 0$, and the angular part of the q operator, $(3 \cos^2 \Theta — 1)$, has highest absolute value at $\cos \Theta — 1$, greater concentration of charge close to $\Theta = 0$ allows an increase in the magnitude of q_{elec}. *Thus the radial and angular effects work in opposite directions.* The

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* One must be very careful about agreements between prediction and experiment: Moccia's 99% prediction of e^2Qq for HCl was solely due to round up errors in the computer.[4,8]

TABLE IV

HCl MO q for OCE-SCF Wavefunctions in the Basis Series Formed by Successively Adding to the GW Basis of ref 7, 9s, 9p, etc. Orbitals with $\zeta = 3.32129$.

MO	q/au									
	GW	GW+1	GW+2	GW+3	GW+4	GW+5	GW+6	GW+7	GW+8	GW+9
1σ	—.00002	—.00002	—.00002	—.00003	—.00004	—.00004	—.00005	—.00005	—.00005	—.00005
2σ	—.00214	—.00211	—.00213	—.00479	—.00455	—.00455	—.00458	—.00460	—.00462	—.00463
3σ	—159.81711	—159.83041	—159.82821	—159.78359	—159.77342	—159.76293	—159.75641	—159.75235	—159.74981	—159.74818
4σ	—.27932	—.27894	—.27928	—.25108	—.23098	—.22292	—.21955	—.21795	—.21713	—.21670
5σ	—8.21412	—8.20252	—8.23275	—7.86197	—7.48301	—7.28938	—7.18000	—7.11492	—7.07493	—7.04966
1π	80.09098	80.09895	80.09529	80.11365	80.12693	80.13523	80.14004	80.14292	80.14469	80.14581
2π	4.94887	4.95051	4.95234	5.01231	5.06159	5.08426	5.09654	5.10373	5.10812	5.11089
Total (q_{total})	1.76700	1.78493	1.75288	2.35045	2.88505	3.15916	3.31257	3.40343	3.45908	3.49418
q_{total}[3] (experimental) =										3.4908au

The basis series is labelled: GW + 1 for 21-orbital basis set consisting of the GW basis plus a 9s orbital with $\zeta = 3.32129$; GW + 2 is the 22-orbital basis from GW + 9s + 9p with $\zeta = 3.32129$ and similarly to GW + 9 which includes the final 9k orbital[1,4,8].

radial effect dominates strongly after the first few additions, Table IV. Qualitatively, the higher angular momentum numbers allow a build-up of charge near the proton by orbitals with the appropriate $r_{\max}$, producing a substantial energy lowering so that these orbitals contribute to the 4σ and 5σ MOs; the radial effect determines the change in q as orbitals are added.

ANALYSIS OF q_{elec} BY ORBITAL-PAIR TYPE

The total q_{elec}, and the q_{elec} of each individual MO, is a sum of terms (1) containing integrals of the form $< \Phi_i \mid \partial^2 V/\partial z^2 \mid \Phi_j >$. The terms can be classified by the pair of angular momentum quantum numbers l_i and l_j of Φ_i and Φ_j. The integral is symmetric in Φ_i and Φ_j. The integral $< \Phi_i \mid \partial^2 V/\partial z^2 \mid \mid \Phi_j >$ has as a factor the angular integral

$$\int_0^{\pi} d\Theta \sin\Theta \int_0^{2} d\Phi \, S_{l_i m_i}(\Theta, \Phi) \, S_{l_j m_j}(\Theta, \Phi) \, S_{20}(\Theta, \Phi) \tag{5}$$

This integral vanishes[1] unless

$$l_i + l_j > 2 \tag{6}$$

and

$$| l_i - l_j | > 2 \tag{7}$$

An additional identity for these integrals[10] implies that (5) vanishes unless $l_i - l_j$ is even. Using this condition, with (6) and (7), the only possible orbital pairs making non-zero contributions to q_{elec} when the highest l-value in the basis is 8 (a k-orbital) are (orbital types to left, l-values in parentheses):

s—d	(0—2)	
p—p	(1—1)	
p—f	(1—3)	
d—d	(2—2)	
d—g	(2—4)	
f—f	(3—3)	
f—h	(3—5)	
g—g	(4—4)	(8)
g—i	(4—6)	
h—h	(5—5)	
h—j	(5—7)	
i—i	(6—6)	
i—k	(6—8)	
j—j	(7—7)	
and k—k	(8—8)	

In Table V the total q_{elec} 's of (1) for the 10 basis sets of Table IV are broken down into contributions from the orbital pairs of (8). The addition of orbitals with higher l greatly affects q_{elec} indirectly, by allowing a more important contribution from the starred 9p orbital to the 5σ MO, rather than

TABLE V

Orbital Pair Analysis, GW Basis Extended with n = 9 *Orbitals,* $r_{max} = 2.4087$ au

Pair type	q_{elec} au			
	GW	GW+9s	GW+9(s+p)	GW+9 (s+p+d)
sd	—0.03514	—0.03498	—0.03496	—0.03329
*pp	1.82154	1.83932	1.80727	2.39271
pf				
dd	—0.01940	—0.01942	—0.01943	—0.01347

Table V, contd.

Pair type	GW+9 (s+p+d+f)	GW+9 (s+p+d+f+g)	GW+9 (s+p+d+f+ +g+h)
sd	—0.02992	—0.02883	—0.02827
pp	2.95952	3.24075	3.39730
pf	—0.02883	—0.03093	—0.03211
dd	—0.01465	—0.01524	—0.01556
dg		—0.00492	—0.00534
ff	—0.00107	—0.00126	—0.00137
fh			—0.00143
gg		—0.00042	—0.00048
hh			—0.00018

Pair type	GW+9 (s+p+d+ +f+g+h+i)	GW+9 (s+p+d+f+ +g+h+i+j)	GW+9 (s+p+d+f+ +g+h+i+j+k)
sd	—0.02797	—0.02780	—0.02770
*pp	3.48981	3.54642	3.58210
pf	—0.03271	—0.03307	—0.03330
dd	—0.01577	—0.01590	—0.01599
dg	—0.00560	—0.00574	—0.00584
ff	—0.00142	—0.00146	—0.00148
fh	—0.00154	—0.00161	—0.00165
gg	—0.00051	—0.00053	—0.00055
gi	—0.00583	—0.00063	—0.00067
hh	—0.00020	—0.00021	—0.00022
hj		—0.00026	—0.00028
ii	—0.00008	—0.00009	—0.00009
ik			—0.00012
jj		—0.00004	—0.00004
kk			—0.00002

directly through orbital pair contributions to q_{elec} involving the higher l quantum numbers. The coefficients of the starred 9p basis orbital to the 5σ MO for the various basis sets in Table VI illustrate this.

TABLE VI

Coefficients of 5σ MO of HCl, GW Series of Bases with $n=9$, $r_{\max} = 2.4087$ *Orbitals Added*

Orbital	Coefficient				
	ζ	GW	GW+9s	GW+9 (s+p)	GW+9 (s+p+d)
1s	18.424	—0.018548	0.018241	0.018248	0.018620
2s	16.187	—0.014398	0.013830	0.013831	0.014080
2s	6.092	0.105325	—0.102304	—0.102324	—0.104287
3s	2.608	—0.276551	0.252747	0.252516	0.255651
3s	1.597	0.071784	—0.026342	—0.025579	—0.021046
2pσ	10.267	—0.046900	0.046899	0.045809	0.044693
2pσ	5.608	—0.201134	0.200903	0.204820	0.200323
3pσ	2.608	0.434062	—0.433388	—0.457930	—0.447645
3pσ	1.463	0.625434	—0.625729	—0.571120	—0.556738
3dσ	1.943	0.161126	—0.161214	—0.161281	—0.108753
9s	3.32129		—0.032493	—0.033424	—0.043202
*9pσ	3.32129			—0.041130	—0.055217
9dσ	3.32129				—0.125341

Table VI, contd.

Orbital	ζ	GW+9 (s+p+d+f+g)	GW+9 (s+p+d+f+g)	GW+9 (s+p+d+f+g+h)
1s	18.424	0.019194	—0.019555	—0.019794
2s	16.187	0.014503	—0.014771	—0.014950
2s	6.092	—0.107464	0.109468	0.110798
3s	2.608	—0.262879	—0.267513	—0.275096
3s	1.597	—0.019942	0.019500	0.019252
2pσ	10.267	0.043436	—0.042789	—0.042419
2pσ	5.608	0.195268	—0.192780	—0.191380
3pσ	2.608	—0.436142	0.430615	0.427518
3pσ	1.463	—0.450786	0.532298	0.527426
3dσ	1.943	—0.115371	0.117557	0.118700
9s	3.32129	—0.050240	0.053561	0.055396
*9pσ	3.32129	—0.069481	0.075991	0.079674
9dσ	3.32129	—0.142362	0.151168	0.155433
9fσ	3.32129	—0.117973	0.127592	0.133176
9gσ	3.32129		0.073848	0.078735
9hσ	3.32129			0.048203

Orbital	ζ	GW+9 (s+p+d+f+g+h+i)	GW+9 (s+p+d+f+g+h+i+j)	GW+9 (s+p+d+f+g+h+i+j+k)
1s	18.424	—0.019948	0.020048	—0.020113
2s	16.187	—0.015064	0.015138	—0.015187
2s	6.092	0.111653	—0.112205	0.112567
3s	2.608	—0.272581	0.273866	—0.274708
3s	1.597	0.019110	—0.019024	0.018969
2pσ	10.267	—0.042197	0.042061	—0.041974
2pσ	5.608	—0.190547	0.190036	—0.189712
3pσ	2.608	0.425682	—0.424557	0.423846
3pσ	1.463	0.524498	—0.522684	0.521532
3dσ	1.943	0.119450	—0.119922	0.120225
9s	3.32129	0.056485	—0.057158	0.057587
*9pσ	3.32129	0.081897	—0.083288	0.084182
9dσ	3.32129	0.157972	—0.159543	0.160545
9fσ	3.32129	0.136021	—0.137776	0.138888
9gσ	3.32129	0.081741	—0.083309	0.084296
9hσ	3.32129	0.050764	—0.052389	0.053252
9iσ	3.32129	0.032270	—0.033651	0.034550
9jσ	3.32129		—0.022175	0.022946
9kσ	3.32129			0.015628

CONTRIBUTION TO q_{elec} OF INNER SHELLS

This effect[11] will be examined later[12] but the 1σ, 2σ, and 1π MO non-zero contributions to q_{elec} corresponding to inner shells of the Cl^- ion, is part of the Sternheimer effect[13,14]. Table VII contains the shell contributions to the

TABLE VII

Shell Analysis of q_{elec}, HCl, GW Basis Series

Shell	GW	GW+9s	GW+9 (s+p)	GW+9 (s+p+d)
1	—0.00002	—0.00002	—0.00002	—0.00003
2	0.36271	0.36538	0.36024	0.43892
3	1.40430	1.41956	1.39265	1.91157

Table VII, contd.

Shell	GW+9 (s+p+d+f)	GW+9 (s+p+d+f+g)	GW+9 (s+p+d+f+g+h)
1	—0.00004	—0.00004	—0.00005
2	0.47589	0.50298	0.51909
3	2.40919	2.65622	2.79353

Shell	GW+9 (s+p+d+ +f+g+h+i)	GW+9 (s+p+d+ +f+g+h+i+j)	GW+9 (s+p+d+f+ +g+h+i+j+k)
1	—0.00005	—0.00005	—0.00005
2	0.52889	0.53495	0.53881
3	2.87459	2.92418	2.95542

total q_{elec} analogous to Table II. For the 29 orbital set including $l = 8$, the contributions from shells 1 and 2 total 0.53876 au compared to a total q_{elec} of 3.49418 au, or 15%,[15] considerably less than the 25% by Moccia's 71-orbital basis and in qualitative agreement with the results of Scrocco and Tomasi[16]. It will be compared with the accurate two-centre calculations of Cade and Huo[17] and of McLean and Yoshimine[18] in the next paper.[19]

CONCLUSION

An effective OCE basis for both energy and the EFG has been developed, which permits a reasonably inexpensive calculation to obtain results comparable to those from a TCE calculation of near H—F accuracy.

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REFERENCES

1. J. E. Grabenstetter and M. A. Whitehead, *Croat. Chem. Acta* **48** (1976) 245.
2. R. Moccia, *J. Chem. Phys.* **40** (1964) 2164, 2186; *Theoret. Chim. Acta* **8** (1967) 8.
3. E. W. Kaiser, *J. Chem. Phys.* **53** (1970) 1686.
4. J. E. Grabenstetter, *Ph. D. Thesis,* McGill University, Canada (1974).
5. E. Clementi, *Tables of Atomic Wavefunctions,* supplement to IBM Journal of Res. and Dev. **9** (1965) 2.
6. P. S. Bagus, *Phys. Rev.* **139** (1965) A619.
7. T. L. Gilbert and A. C. Wahl, *J. Chem. Phys.* **55** (1971) 5247.
8. J. E. Grabenstteter and M. A. Whitehead, *Can. J. Chem.* **54** (1976) 1948.
9. G. Birkoff and G. C. Rota, *Ordinary Differential Equations,* Blaisdell, Waltham, Mass., 2nd edition, 1969, p. 60.
10. E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra,* Cambridge University Press, 1935, p. 176.
11. M. A. Whitehead, *Proceedings of the Second International Symposium on NQR Spectroscopy,* A. Colligiani (Ed.), Vallerini, Pisa, Italy, (1975) p. 27.
12. J. E. Grabenstetter and M. A. Whitehead, *J. C. S. Faraday II,* **74** (1978) 1.
13. R. Sternheimer, *Phys. Rev.* **80** (1950) 102.
14. R. Sternheimer, *Phys. Rev.* **84** (1951) 244.
15. J. E. Grabenstetter and M. A. Whitehead, *Chem. Phys. Lett.* **37** (1976) 547.
16. E. Scrocco and J. Tomasi, *Theoret. Chim. Acta* **2** (1964) 386.
17. P. E. Cade and W. M. Huo, *J. Chem. Phys.* **47** (1967) 649.
18. A. D. McLean and M. Yoshimine, *J. Chem. Phys.* **47** (1967) 3256.
19. J. E. Grabenstetter and M. A. Whitehead, *Mol. Phys.* **34** (1977) 1577.

SAŽETAK

Računi samousklađenog polja na molekuli HCl metodom razvoja valne funkcije na jednom centru. Dio II. Analiza gradijenta električkog polja izračunanog s pomoću valne funkcije jednog centra kod jezgre atoma klora

J. E. Grabenstetter i M. A. Whitehead

Gradijent električkog polja na mjestu jezgre atoma klora u molekuli HCl izračunan je s pomoću valne funkcije jednog centra dobivene metodom samousklađenog polja a sastoji se od 29 orbitala. Teorijska vrijednost dobro se slaže s eksperimentom. Diskutiran je utjecaj kvalitete upotrijebljenih funkcija osnovnog skupa na izračunane molekularne orbitale. Analiza pokazuje da osnovni skup funkcija Moccia koji ima 71-atomsku orbitalu ne opisuje drugu elektronsku ljusku na zadovoljavajući način.

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