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Self Consistent Modified Extended Hückel (SC–MEH) Calculations on Heavy Metal Systems. I. Platinum(II) Tetragonal Planar Complexes With and Without Relativistic Effects*

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The Self Consistent Modified Extended Hückel molecular orbital method had been applied to several square planar complexes of platinum (II). Calculations including both the limited 5*d*, 6*s*, 6*p* and extended 5*s*, 5*p*, 5*d*, 6*s*, 6*p* starting bases for platinum were made. It is shown that in $PtCl_4^{2-}$ both the nuclear quadrupole moment and minimum total energy vs. bond distance are calculated to be in good agreement with experiment, only with the extended platinum AO basis.

Specific inclusion of relativistic parameters via a pseudo-relativistic approximation are shown to have a significant effect on the energy molecular energy levels, however no meaningful rationalization can be made without the simultaneous inclusion of ligand field parameters as well.

Key words: Heavy metal systems, Self Consistent Modified Extended Hückel calculations on ~–Platinum(II) tetragonal planar complexes.

1. Introduction

Several publications have appeared recently wherein the authors have sought to include relativistic effects into the quantum mechanical description of bonding in heavy metal complexes [1–3]. This approach has been further facilitated by the timely publication of HF-SCF relativistic atomic wave functions and their related parameters [4–6].

The work of Bersuker *et al.* [1] is particularly important in the development of relativistic semi empirical MO calculations, but was primarily concerned with

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introducing the formalism for incorporating relativistic factors into Extended Hückel (EH) type of calculations using $PtCl_6^{2-}$ as an example. The work reported herein extends the pseudorelativistic semiempirical MO technique to include several Pt(II) tetragonal complexes with complete computational details.

The Self Consistent Modified Extended Hückel (CS-MEH) MO method, for which it has already been amply demonstrated as being capable of producing quite reliable results [7–9], has been applied with the pseudo-relativistic modifications proposed by Bersuker et al. [1] to the Pt(II) complexes: I-$PtCl_4^{2-}$, II-*cis*-$Pt(NH_3)_2Cl_2$, III-*trans*-$Pt(NH_3)_2Cl_2$, IV-$Pt(NH_3)_4^{2+}$ and V-$Pt(CN)_4^{2-}$, (hereafter designated I, II, III, IV and V). A preliminary set of SC-MEH calculations was made in which none relativistic atomic parameters were employed. This was augmented by a second set of calculations using pseudo-relativistic orbitals, which included both relativistic and ligand field perturbations derived in a manner to be described.

2. Computational Procedure

It is important to point out that the SC-MEH MO method is not just the usual EH type of method. It differs in significantly the following manner:

(1) Löwdin orthogonalization is used exclusively. This has the advantage that all the AO's within an MO are orthogonal to each other, and by a least squares criterion the Löwdin orbitals are the closest to the original set of orbitals of all possible orthogonal sets. It has been shown that this leads to a significantly more reliable derivation of the population and charge analysis [7–8].

(2) The molecular Hamiltonian is so partitioned that the environmental molecular factors may be systematically incorporated in an additive manner [7–8]. Thus second order effects (i.e. spin-orbit, ligand field, etc.) may be adequately accounted for by either incorporating them directly into the self consistent iterative routine, or by treating them as perturbations to the initial eigenvectors and reiterating to self consistency [7–9]. Either approach provides essentially the same results at least as far as second order effects in the ground state are concerned.

2.1. Wavefunctions

Single exponential Slater type orbitals (STO's) which are properly gauged to provide accurate overlaps were utilized in these studies. Atomic spin-orbital parameters, $\langle r\rangle$ and $\langle r^2\rangle$, attained from recent relativistic (Dirac–Fock) neutral-atom calculations [4] were employed in the determination of the optimal single ζ STO's used in the calculations. Plots of ζ versus n for each relativistic spin-orbital were made using the following Eqs.:

$$\begin{aligned} \zeta &= \frac{n+1/2}{\langle r\rangle} \\ \zeta &= \frac{(2n+2)(2n+1)^{1/2}}{4\langle r^2\rangle}. \end{aligned} \tag{1}$$

Table 1. Relativistic Orbital Exponents

Atom	Orbital	n	ζ-Value
Platinum	$5s$(N.R.)	2	2.62430
	$5p$(N.R.)	2	2.27918
Platinum	$5d^*$	2	1.55265
	$5d$	2	1.47275
	$5d$(N.R.[a])	2	1.50471
	$6s$($6s$ N.R.)	3	1.11704
	$6p^*$	3	0.69967
	$6p$	3	0.62127
	$6p$(N.R.)	3	0.64921
Chlorine	$3s$	2	1.62594
	$3p^*$	2	1.36316
	$3p$	2	1.35630
	$3p$(N.R.)	2	1.35859
Nitrogen	$2s$	2	1.88288
	$2p$	2	1.69621
Carbon	$2s$	2	1.57470
	$2p$	2	1.41152
Hydrogen	$1s$	1	1.00000

[a] N.R. denotes "Non-Relativistic," calculated according to Eq. (2).

The n and ζ pair which best fits the two relations for a particular spin-orbital was chosen, with the stipulation that all orbitals on a particular type of atom which are involved in bonding are given the same n-value. The results of this procedure are provided in Table 1. (In this Table and hereafter, * denotes the $j=l-1/2$ spin-orbital, and the absence of * denotes the $j=l+1/2$ spin-orbital.)

As the preliminary calculation required standard orbitals, a method was developed (see Appendix 1) whereby non-relativistic (Russell–Saunders) orbitals (denoted N.R.) could be derived from the relativistic spin-orbitals:

$$\begin{aligned}\psi p(\text{N.R.}) &= 1/3\psi p^* + 2/3\psi p\\ \psi d(\text{N.R.}) &= 2/5\psi d^* + 3/5\psi d\end{aligned} \tag{2}$$

where the averaging is applied to Pt and Cl but not the other atoms since spin-orbit coupling is minimal in the latter. We have adopted this approach rather than invoke non-relativistic HF-SCF atomic parameters from alternate sources, so that any extenuating complications that might otherwise arise via the use of mixed basis sets would be avoided. Furthermore, a comparison between these derived orbitals and the non-relativistic HF-SCF atomic orbitals obtainable from other sources reveals a great similarity between the two, thus substantiating the validity of the approach.

For platinum(II), it is necessary to generate compatible orbital exponents for the unfilled virtual orbitals $6p^*$, $6p$, and $6s$. Since the $6p$ orbitals are not computed in the published neutral-atom relativistic calculations [4–6], the necessary data ($\langle r\rangle$ and $\langle r^2\rangle$) were extrapolated from atoms of higher atomic number (i.e. Ra, At, Po, Bi, Pb and Tl) down to platinum, via a quadratic least squares curve, as shown in Fig. 1a and 1b. The optimal ζ values were then computed according to the procedure described above.

2.2. Orbital Energies

The Hamiltonian diagonal matrix elements, H_{ii}, were computed according to the formula

$$H_{ii} = \text{I.P.} + \text{E.A.} - \text{F} + \text{E.L.} \tag{3}$$

where I.P. is the ionization potential of the i^{th} atomic orbital (extracted from Ref. [10]), E.A. is the corresponding electron affinity, and F is a ligand

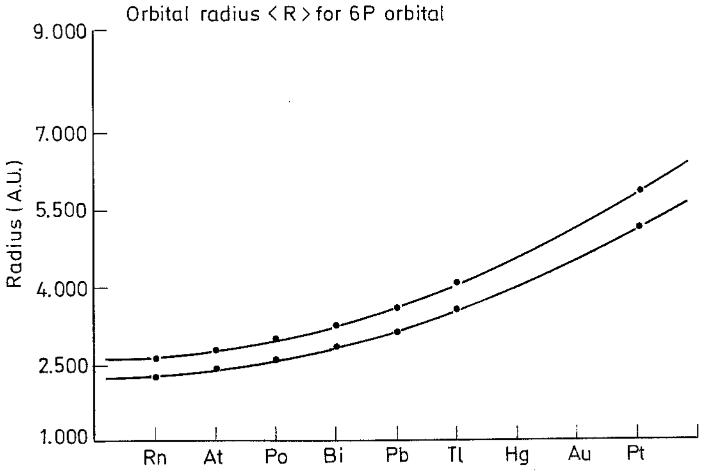

Fig. 1a. Orbital parameter $\langle r\rangle$ for 6p orbital, Ra to Pt

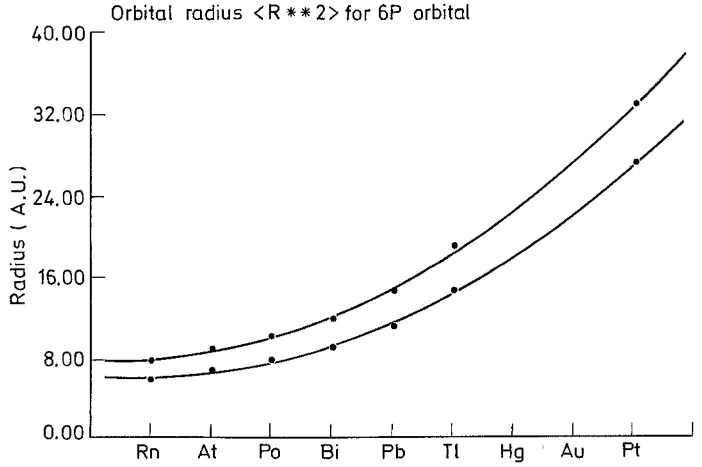

Fig. 1b. Orbital parameter $\langle r^2\rangle$ for 6p orbital, RA to Pt

delocalization factor, and E.L. are atomic electrostatic terms. The I.P., E.A. and F terms relate to the VOIE portion of H_{ii}, which is here approximated in a manner quite analogous to that of well known CNDO methods. The electron affinities were calculated according to the method of Hinze and Jaffe (zero charge) of assumed equal to the I.P. of the charge minus one state for charges 1, 2, and 3. For platinum 5*s* and 5*p*, E.A. and F were assumed to be zero. The ligand delocalization factor, the average electron affinity of the ligands, was introduced to account for variations in the orbital energy according to the oxidizing power of the ligand atom. Finally, data for atom charges 0, 1, 2, and 3 were fitted to a quadratic equation $H_{ii} = AQ^2 + BQ + C$. The A, B, and C values used are given in Table 2. For the ligand H_{jj}, F was taken to be the electron affinity of platinum (20.645*kk*, Ref. [13]). It should be noted that with this scheme significantly different platinum H_{ii} values may occur depending on the ligands used.

The off-diagonal elements, H_{ij}, and various intra molecular potential terms were handled as described previously [7-9].

3. Preliminary Calculations

SC-MEH calculations were performed on molecular clusters I, II, III, IV, and V. Two different platinum basis sets were utilized for comparative purposes: 5*d*, 6*s*, and 6*p* (basis 1) and 5*s*, 5*p*, 5*d*, 6*s* and 6*p* (basis 2). The calculations

Table 2. Atomic Orbital Energies

Atom	Orbital	A	B	C
Nitrogen	2*s*	65.802	228.060	293.893
	2*p*	60.894	191.560	102.938
Chlorine	3*s*	36.754	103.837	309.490
	3*p*	25.0318	202.332	148.936
Hydrogen	1*s*	221.056	213.013	115.417
Platinum	5*s*	0.0	108.31	875.53
	5*p*	0.0	106.47	507.386
	5*d*	19.205	169.383	72.268
($PtCl_4^{2-}$)	6*s*	12.2825	138.8175	87.7675
Platinum	6*p*	9.365	116.203	32.518
	5*s*	0.0	108.31	875.53
	5*p*	0.0	106.47	507.386
	5*d*	20.615	175.457	11.122
($Pt(NH_3)_4^{2+}$)	6*s*	8.089	167.528	6.426
Platinum	6*p*	10.826	121.683	−28.614
	6*s*	0.0	108.31	875.53
	5*p*	0.0	106.47	507.386
	5*d*	23.505	157.95	63.154
($PtCl_2)NH_3)_2$)	6*s*	10.978	150.027	58.461
	6*p*	13.667	104.263	23.413
Carbon	2*s*	56.013	250.245	108.113
	2*p*	58.207	172.787	63.978

were iterated until a charge self-consistency of ≤ 0.0001 charge unit was obtained. Some numerical results are given in Table 3a, b, c and Fig. 2.

There are not many observable properties of Pt(II) systems that can be calculated with any degree of reliability without invoking explicit consideration of the excited states. In addition to the nuclear quadrupole moment of $PtCl_4^{2-}$, the variation in total energy with Pt-Cl distance compared to the observed

Table 3a. Comparative Preliminary Results[a] ($PtCl_4^{2-}$)

C.H.[b]		B.G.[c]		K.[d]		I.M.[e]		M.W.J.[f]		C.B.[g]	
A^*_{2u}	−4.70	A^*_{2u}	−3.56	B^*_{2g}	−6.11	A^*_{2u}	−4.74	A^*_{1g}	−1.4	A^*_{2u}	−1.65
B^*_{1g}	−6.76	B^*_{1g}	−8.02	B^*_{1g}	−6.66	B^*_{1g}	−6.91	B^*_{1g}	−2.8	B^*_{1g}	−2.71
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B_{2g}	−10.49	B_{2g}	−11.59	A_{1g}	−9.26	B_{2g}	−10.53	B_{2g}	−5.8	B_{2g}	−8.71
E_g	−10.68	E_g	−12.27	E_g	−10.44	E_g	−10.71	E_g	−6.0	E_g	−9.05
A_{1g}	−10.98	A_{1g}	−13.24	A_{1g}	−11.97	A_{1g}	−10.99	A_{2g}	−6.2	A_{1g}	−10.06
B_{1g}	−13.49	B_{2u}	−13.68	E_u	−12.18	A_{2g}	−13.59	E_u	−6.5	E_u	−10.91
E_u	−13.83	A_{2g}	−13.69	A_{2g}	−12.64	E_u	−13.92	A_{1g}	−6.6	B_{2u}	−11.61
				B_{2u}				B_{2u}	−6.7		
									−6.8		

[a] All values in eV (----) denotes highest occupied (HOMO)/lowest unoccupied (LUMO) MO separation.

[b] Cotton and Harris (Ref. [16]) – EH calculation.

[c] Basch and Gray (Ref. [15]) – EH calculation.

[d] Kovarskaya (Ref. [18]) – EH calculation.

[e] Interrante and Messmer (Ref. [17]) – EH calculation.

[f] Messmer, Wahlgren and Johnson (Ref. [19]) – SCF-Xα calculation. Data estimamated from Fig. 1 of Ref. [19].

[g] Carsey and Boudreaux (this work) – SC-MEH calculation; basis set 2 (i.e. Pt 5*s*, 5*p*, 5*d*, 6*s* and 6*p*).

Table 3b. Results of Preliminary Calculation[a], basis 2[b]

I (D_{4h})		II (C_{2v})		III (D_{2h})		IV (D_{4h})		V (D_{4h})	
A_{1g}	26.414	A_2	7.601	B_{2u}	7.732		7.485	B_{2u}	−3.330
E_u	14.035	B_2	5.966	B_{3u}	6.695	E_u	6.036	E_u	−3.531
A_{2u}	−1.654	gB_2	−1.885	B_{1u}	−1.855	A_{2u}	−0.532	B_{2u}	−3.977
B_{1g}	−2.708	B_1	−2.584	A_g	−2.584	B_{1g}	−2.251	A_{2u}	−3.977
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B_{2g}	−8.708	A_1	−8.241	B_{2u}	−8.948	B_{2g}	−9.813	E_u	−5.098
E_g	−9.050	A_1	−8.735	B_{3g}	−9.031	E_g	−10.177	A_{1g}	−6.631
A_{1g}	−10.060	A_2	−8.812	B_{1g}	−9.033	A_{1g}	−10.366	B_{2g}	−7.030
E_u	−10.905	A_2	−8.917	B_{2g}	−9.827	E_u	−11.706	E_g	−7.108
B_{2u}	−11.611	B_2	−8.923	A_g	−10.088	A_{1g}	−14.069	A_{1g}	−7.284
		B_1	−9.242	B_{3u}	−10.634			B_{1g}	−7.519
		A_1	−10.345	B_{1u}	−10.731				
		A_2	−10.750	B_{1g}	−10.997				
		A_1	−10.901	B_{1g}	−11.085				
		B_2	−10.919	B_{3g}	−11.884				

[a] (----) denotes highest occupied (HOMO)/lowest unoccupied (LUMO) MO separation.

[b] 5*s*, 5*p*, 5*d*, 6*s*, 6*p* of Pt.

Table 3c. Preliminary Calculation Results (continued) Atomic Charges, basis 1

Atom	I	II	III	IV	V
Pt	+0.141	+0.348	+0.346	+0.695	+0.387
Cl	−0.535	−0.443	−0.450	—	—
N	—	−0.274	−0.274	−0.286	−0.641
C	—	—	—	—	0.440
H	—	~+0.170	~+0.180	+0.204	—
Atomic Charges, basis 2					
Pt	+0.066	+0.264	+0.265	+0.620	+0.290
Cl	−0.516	−0.447	−0.437	—	—
N	—	+0.233	−0.238	−0.261	−0.646
C	—	—	—	—	+0.074
H	—	+0.183	+0.181	+0.202	—

Nuclear Quadrupole moment values (eqQ, mc/sec)

$PtCl_4$, basis 1	26.39
$PtCl_4$, basis 2	32.45
Experimental value [21]	36.1.

crystallographic equilibrium bond distance of 4.36158 a.u., was computed and presented in Figs. 3a, b. Similarly, electron density plots for $PtCl_4^{2-}$ in both bases were made and are given in Figs. 4a, b. Since these are intended merely to display the qualitative features for the two basis sets, no numerical details regarding the electron density contours are included.

The whole purpose of these data is to demonstrate that the SC-MEH method is indeed capable of treating heavy metal systems such as platinum even in the absence of the pseudo-relativistic modification. Further discussion of these results is presented later in Sect. 5.

4. Pseudo-Relativistic Calculations (PRSC-MEH)

A modification of SC-MEH routine at this point allows the calculation of orbitals in the double point group symmetry. This modification required several steps, as will not be delineated:

4.1. Input Data

Since only platinum exhibits significant spin-orbit coupling, relativistic effects were considered for a platinum atom only. Here, it was possible to incorporate a double set of *d* and *p* orbitals in approximation to the four spin-orbitals $5d^*$, $5d$, $6p^*$, and $6p$. Relativistic orbital exponents previously generated (Table 1) were used. The atomic orbital energies listed in Table 2 were employed and the relativistic energy splitting obtained from the neutral atom HF-SCF calculations were incorporated into the *C* term of the VOIE [12]. For platinum, the energy difference $E6p^* - E6p$ was found to be zero by extrapolation as shown in Fig. 5.

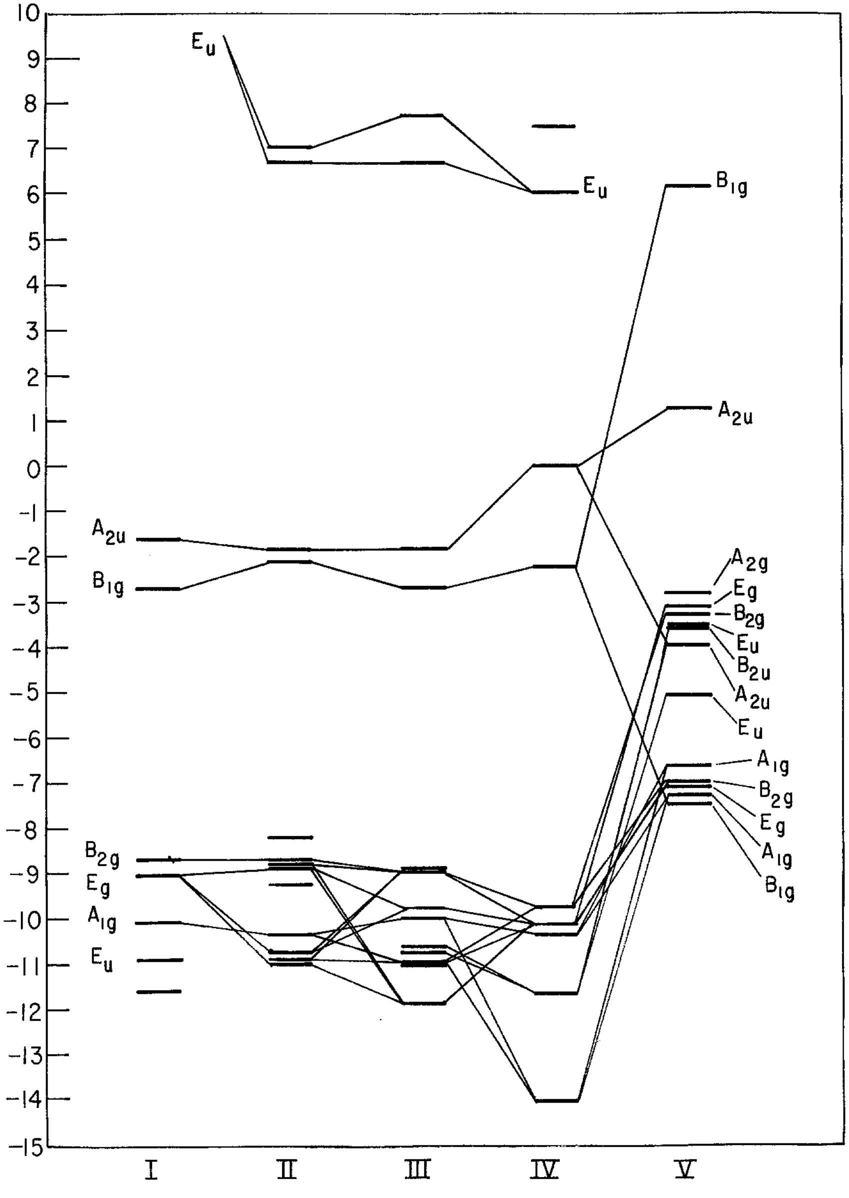


Fig. 2. Computed molecular orbital energies and symmetries from preliminary calculation, basis 2.

Abcissa – I: $PtCl_4^{2-}$
II: *Cis*-$Pt(NH_3)_2Cl_2$
III: *Trans*-$Pt(NH_3)_2Cl_2$
IV: $Pt(NH_3)_4^{2+}$
V: $Pt(CN)_4^{2-}$

Ordinate – Energy (eV)

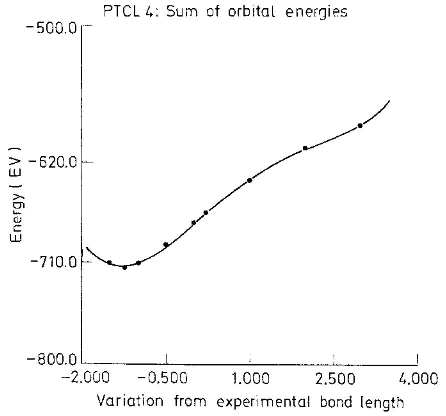


Fig. 3a. Variation of total energy of $PtCl_4^{2-}$ with platinum-chloring distance, basis 1

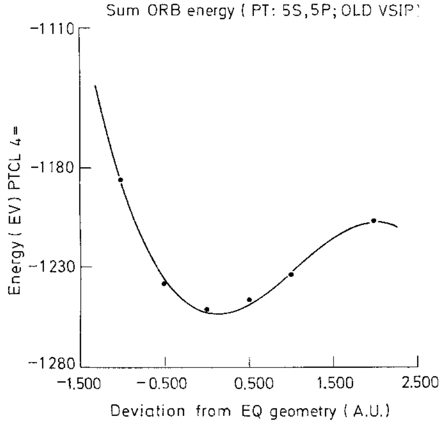


Fig. 3b. Variation of total energy of $PtCl_4^{2-}$ with platinum-chlorine distance, basis 2

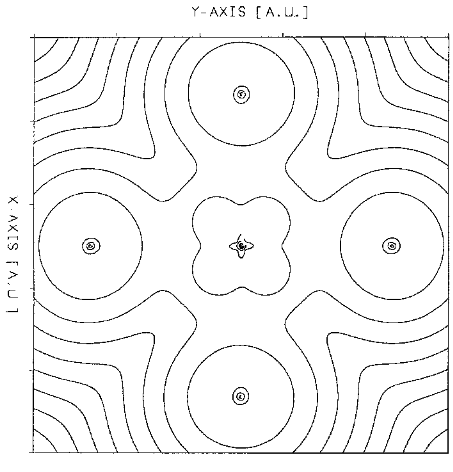


Fig. 4a. Electron density contours for $PtCl_4^{2-}$, basis 1

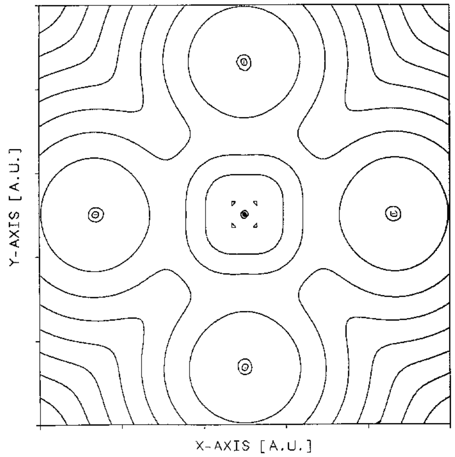


Fig. 4b. Electron density contours for $PtCl_4^{2-}$, basis 2

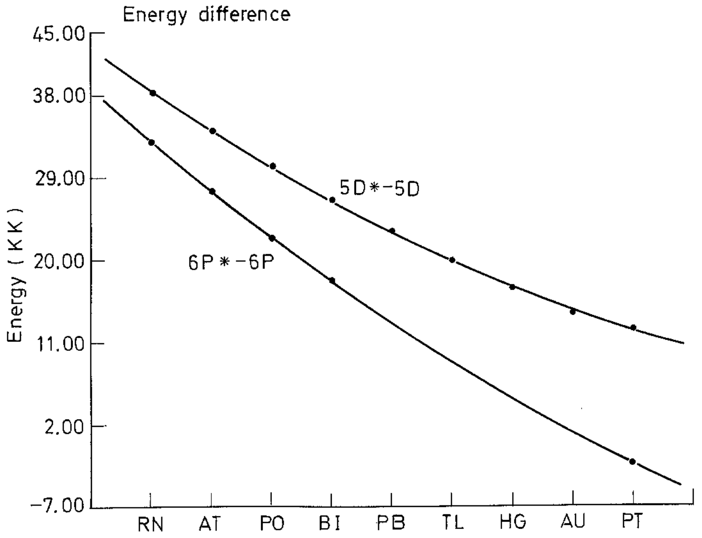


Fig. 5. Energy difference between relativistic orbitals of 3rd row transition elements

Since the original inputs do not contain any orbital spin index, there is no way to attain a self consistency in charge and configuration over spin-orbitals per se. What was required is that the charges from the preliminary calculation, without the need of attaining a new charge self-consistency.

4.2. Modification of Output

4.2.1. Ligand Field Correlation

As remarked earlier, one asset of the SC-MEH MO method is that second order perturbations may be applied subsequent to the self consistent routine without any substantial loss in accuracy. Hence ligand field perturbations were

Table 4. Ligand field perturbation expressions in tetragonal planar symmetry

d_{z^2}	$E=-4/7\frac{\bar{r}^2}{a^3}-3/7\frac{\bar{r}^4}{a^5}$
$d_{xz}. d_{yz}$	$E=-2/7\left(\frac{\bar{r}^2}{a^3}+\frac{\bar{r}^4}{a^5}\right)$
$d_{x^2-y^2}$	$E=\frac{+4}{7}\frac{\bar{r}^2}{a^3}+\frac{19}{21}\frac{\bar{r}^4}{a^5}$
d_{xy}	$E=4/7\frac{\bar{r}^2}{a^3}-\frac{16}{21}\frac{\bar{r}^4}{a^3}$
p_x, p_y	$E=2/5\frac{\bar{r}^2}{a^3}$
p_z	$E=-4/5\frac{\bar{r}^2}{a^3}$

$$\sigma=\frac{\bar{r}^2/a^3}{\bar{r}^5/a^5}=2.717\ (5d)$$
$$=3.109\ (5d^*)$$

calculated for the resultant $l-1/2$ and $l+1/2$ pseudo-relativistic orbitals utalizing the neutral atom relativistic data from Ref. [4]. The electrostatic splitting terms appropriate to tetragonal planar symmetry are listed in Table 4.

The ligand field splitting correction was applied to each molecular orbital, and weighted according to the contribution of each AO in the LCAO-MO with the relation

$$E_i'=E_i+\sum_{i=1}^{j}C_{ij}(Pop_j)(E_{jj})$$

where E_i represents the uncorrected energy for the i^{th} MO, j is the d-orbital designation (i.e., $j=3/2$, for $5d^*$, $j=5/2$ for $5d$), *Pop* is the Löwdin population of this orbital, and E_{jj} is the calculated ligand field correction (Table 4).

4.2.2. Construction of D_{4h}'-Symmetry Orbitals

The construction of pseudo-relativistic molecular orbitals in D_{4h}' symmetry was effected in the following way. The coefficients of the molecular orbitals which referred to the platinum relativistically split atomic orbitals were summed in the same proportion in which relativistic orbitals contain the non-relativistic orbitals (see Appendix).

4.2.3. Energies of D_{4h}' Molecular Orbitals

The calculation of precursor d^*, d, p^* and p orbitals results in a doubling of the symmetry related MO's in the bonding region (two B_{2g} orbitals, etc.) and the corrected energies of the molecular orbitals is made with the reasonable assumption that the major relativistic contributors to the MO's are from the platinum atomic orbitals. Since these atomic orbitals have been split by

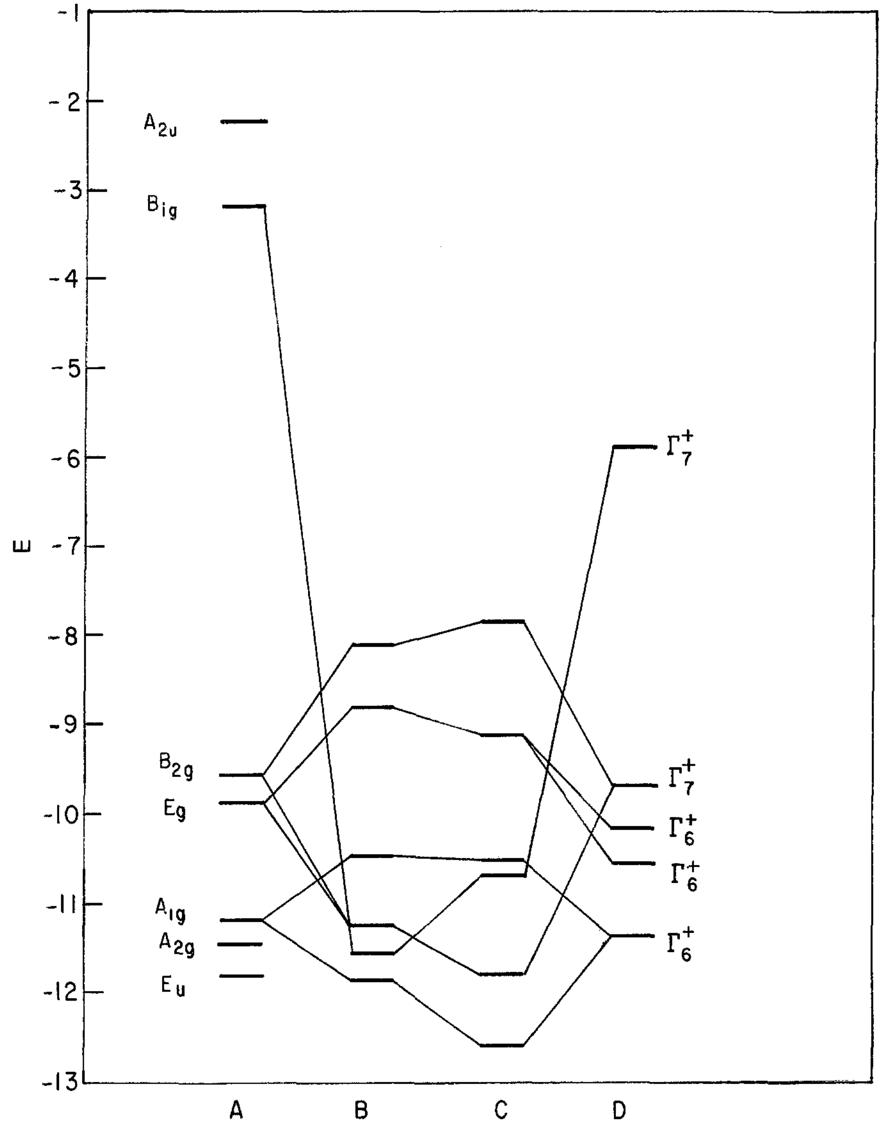


Fig. 6a. Development of pseudo-relativistic molecular orbital energies for $PtCl_4^{2-}$, basis 1.

Abcissa – A: Non-relativistic
B: Relativistic only
C: Relativistic plus ligand field
D: Net effect

Ordinate – Energy (eV)

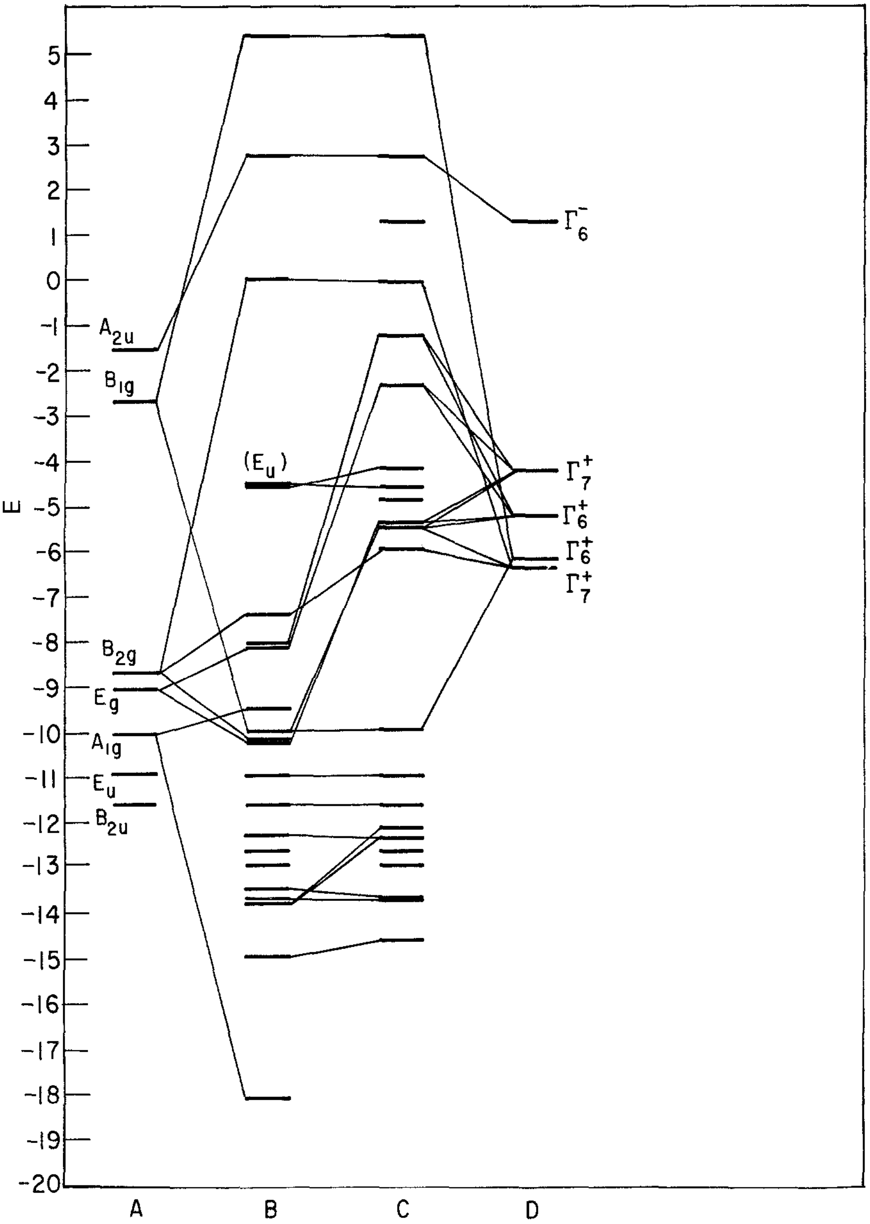


Fig. 6b. Development of pseudo-relativistic molecular orbital energies for $PtCl_4^{2-}$, basis 2.

Abcissa – A: Non-relativistic
B: Relativistic only
C: Relativistic plus ligand field
D: Net effect

Ordinate – Energy (eV)

relativistic effects, we may compute an energy contribution from each AO by summing the energy of the MO in which it resides, multiplied by the coefficient for that AO, i.e.

$$E'_j = \sum_{i=1}^{j} C'_{ij} E'_i$$

where E'_j is corrected energy for the $D_{4h'}$ MO, E'_i is the energy of the ligand field corrected MO, and C'_{ij} is the adjusted (Pseudo-relativistic) coefficient described in the previous section. The effects of each of these corrections on the eigenvalues of $PtCl_4^{2-}$ are diagrammed in Figs. 6a,b for the basis sets 1 and 2.

4.2.4. Pseudo-Relativistic Results

If we assume a summation over spin (as "frozen spin" summation) we may arrive at "average spin – one electron" orbitals as follows:

$$d' = 2/5 d^*_{3/2} + 3/5 d_{5/2} \quad \text{for all } d \text{ orbitals}$$

$$p' = 1/3 p^*_{1/2} + 2/3 p_{3/2} \quad \text{for all } p \text{ orbitals.}$$

This same proportioning was used in the generation of Slater exponents (Eq. 2). A slightly different method is required for output modification into pseudo-relativistic form. The E_g orbitals in the D_{4h} group are split by spin-orbit coupling into a Γ_6^+ and Γ_7^+ for both $d^*_{3/2}$ and $d_{5/2}$. Analysis of the proportionality indicates that

$$E_g\colon \quad \Gamma_7^+ = 1/5 d^*_{3/2} + 4/5 d_{5/2}$$

$$\Gamma_6^+ = 3/5 d^*_{3/2} + 2/5 d_{5/2}$$

$$\text{others:} \quad \Gamma_{6,7}^+ = 2/5 d^*_{3/2} + 3/5 d_{5/2}.$$

This proportionation was used for the construction of pseudo-relativistic molecular orbitals and their energies as described earlier in this section. The final results are presented in Table 5 and Figs. 7a,b, for the two basis sets.

Table 5. PRSC-MEH Results

	Valence orbital energy (eV)				
D'_{4h} Symmetry	I	II	III	IV	V
Basis 1					
Γ_6^-	−4.170	−3.832	−1.824	0.565	0.290
Γ_7^+	−5.874	−7.868	−9.008	−4.409	+9.543
Γ_7^+	−9.670	−14.900	−12.790	−10.539	−7.671
Γ_7^+	−10.144	−16.944	−17.263	−11.677	−8.834
Γ_6^+	−10.523	−14.875	−13.533	−12.184	−9.534
Γ_6^+	−11.343	−15.670	−15.234	−12.191	−9.523
Basis 2					
Γ_7^+	−6.174	−12.780	−13.495	−3.784	+9.103
Γ_7^+	−6.347	−10.156	−13.639	−6.917	−5.130
Γ_7^+	−4.212	−11.017	−8.058	+0.642	−0.124
Γ_6^+	−5.183	−8.794	−6.930	−0.143	−1.391
Γ_6^+	−20.323	−23.557	−20.120	−23.703	−20.226

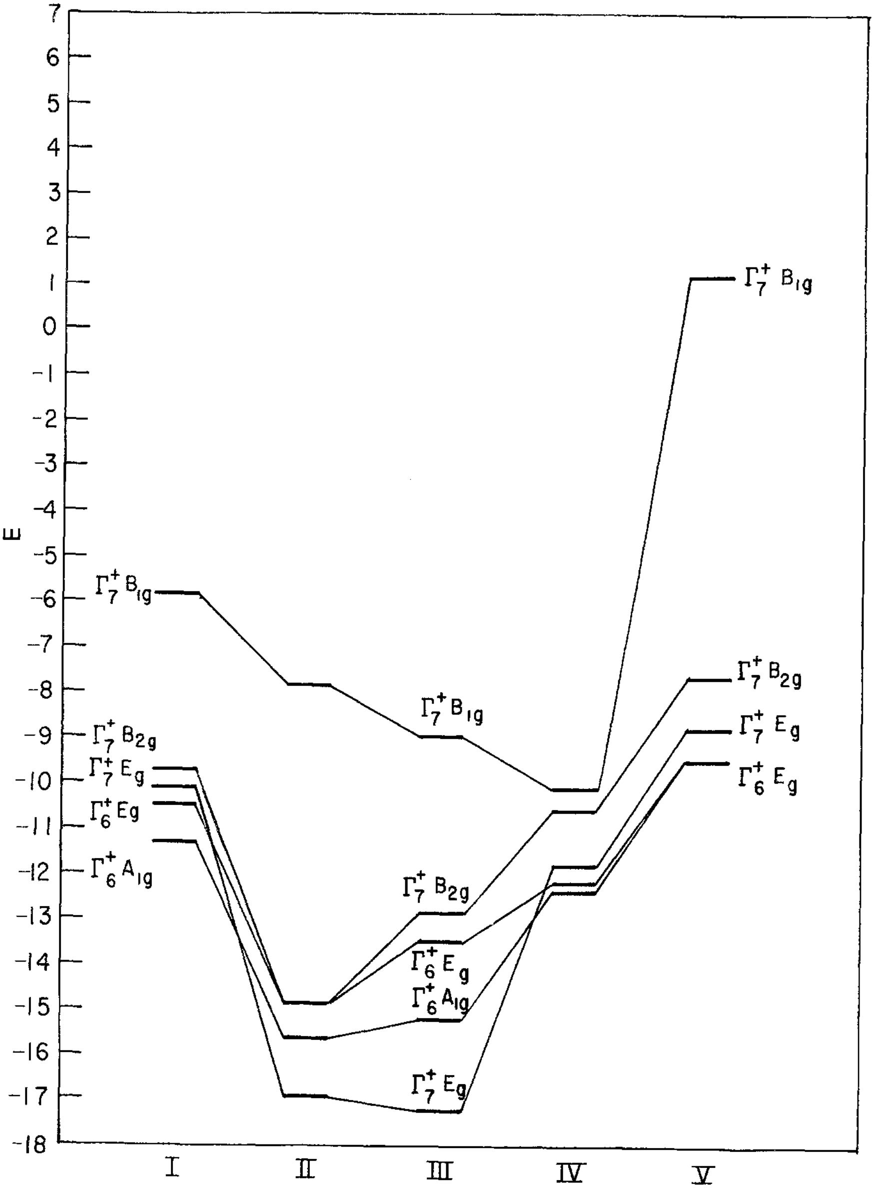


Fig. 7a. Pseudo-relativistic molecular orbitals and symmetries for I–V basis 1.

Abcissa – I: $PtCl_4^{2-}$
II: *Cis*-$Pt(NH_3)_2Cl_2$
III: *Trans*-$Pt(NH_3)Cl_2$
IV: $Pt(NH_3)_4^{2+}$
V: $Pt(CN)_4^{2-}$

Ordinate – Energy (eV)

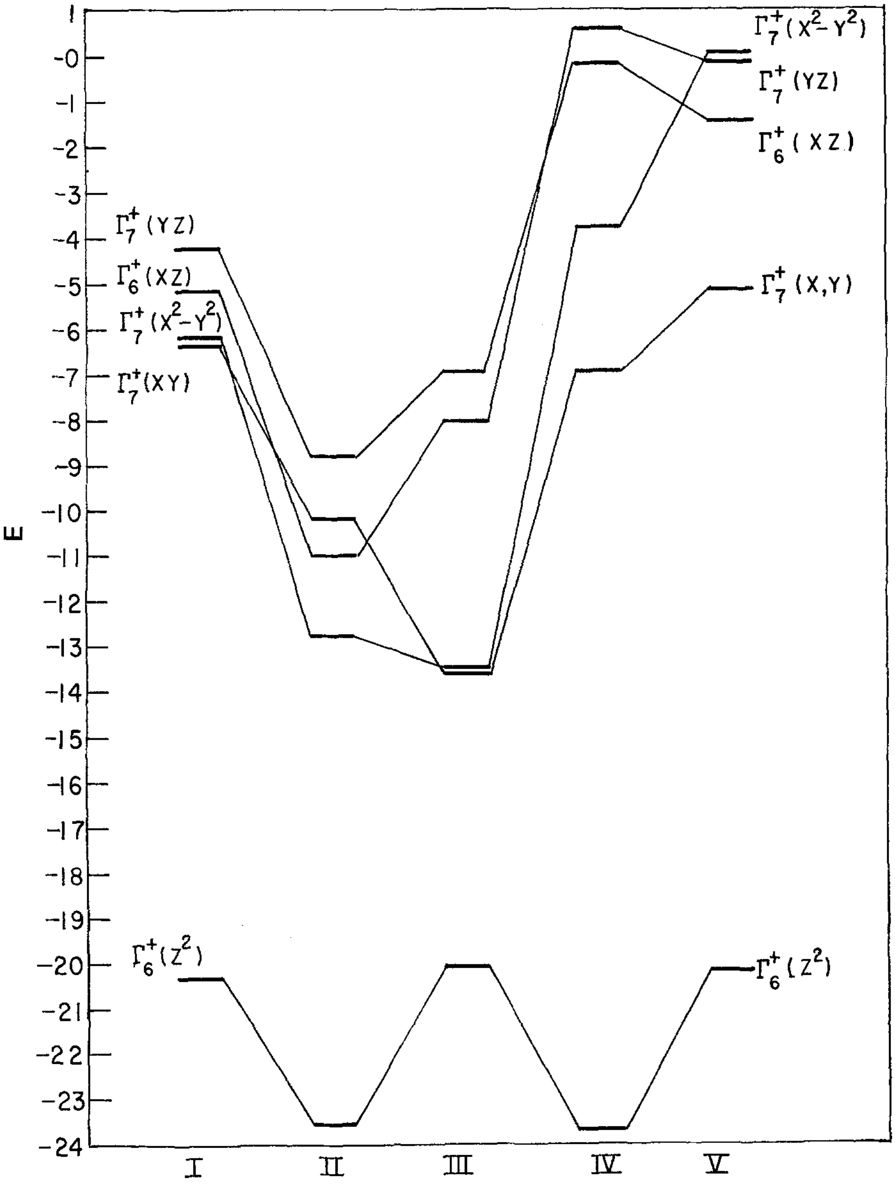


Fig. 7b. Pseudo-relativistic molecular orbitals and symmetries for I–V basis 2.

Abcissa – I: $PtCl_4^{2-}$
II: *Cis*-$Pt(NH_3)_2Cl_2$
III: *Trans*-$Pt(NH_3)_2Cl_2$
IV: $Pt(NH_3)_2^{2+}$
V: $Pt(CN)_4^{2-}$

Ordinate – Energy (eV)

5. Discussion and Conclusion

5.1. *Molecular Orbitals and Energies*

The relative ordering of the predominantly platinum valence-shell molecular orbitals with basis 1 is $\Gamma_6^-(\mathrm{A}_{2u}) > \Gamma_7^+(\mathrm{B}_{1g}) > \Gamma_7^+(\mathrm{B}_{2g}) > \Gamma_7^+(\mathrm{E}_g) > \Gamma_6^+(\mathrm{E}_g) > \Gamma_6^+(\mathrm{A}_{1g})$ for PtCl_4^{-2}, which as shown in Table 3a is similar to most previously published non-relativistic EH calculations [15–18].

A comparison of the present work with that of the SCF-Xα calculation [19] shows that the ordering in the basis 2 MO levels of PtCl_4^{2-} is the same, with the exception of the conspicuous A_{2g} level, which is present in the SCF-Xα results. It is important to note that the only allowed electronic transition from the A_{2g} level is to the A_{2u}^* (ligand π to metal p charge-transfer) in the z direction. However, the symmetry of this transition would be ${}^1A_{2g}$ (i.e. $A_{2g} \otimes A_{2u} \otimes A_{2u} = A_{2g}$) and hence forbidden. Thus the SCF-Xα results are at variance with the experimental data on this point, as an optical transition is observed in the 5.4–5.7 eV range having a molar extinction coefficient of 9,600. This dilemma is apparently resolved in the relativistic context, as the symmetry of the transition becomes ${}^1\Gamma_6^+$ and is fully allowed. Yet, the problem remains that the pseudo-relativistic SC-MEH calculation results in a $\Gamma_2^+(A_{2g}) - \Gamma_2^-(A_{2u})$ energy separation of more than 11 eV. While the SC-MEH results are at variance with those of the SCF-Xα by a maximum deviation of some 3–6 eV (see Table 3a) the variation could in no way be three times greater than this.

5.2. *Energy Minima*

It is known that the sum of orbital energies computed by the Extended Hückel technique often show minima at the experimentally determined bond distances for molecules containing light atoms [20]. In these calculations, the minimum for PtCl_4^{2-} was exactly predicted from data using basis 2, while with basis 1 it was too short by approximately 1.5 a.u. (0.8 Å) (see Figs. 3a,b). Although not involved significantly in bonding, the platinum 5s and 5p orbitals do have a significant effect on the total energy and hence on the energy vs. bond distance relation.

5.3. *Nuclear Quadrupole Moment*

The eqQ values for PtCl_4^{2-} previously published described using basis sets 1 and 2 differ considerable. In the latter the accuracy is 90% of the experimental value, but only 73% for the former. The platinum inner orbitals again show considerable effect on the result.

5.4. *Atomic Charges*

Both basis sets predict low platinum charges in PtCl_4^{2-}, but does become increasingly more positive with positive molecular charge, as expected. Unfortunately, there is no reasonable means of attaining experimental verification of this charge calculation at present.

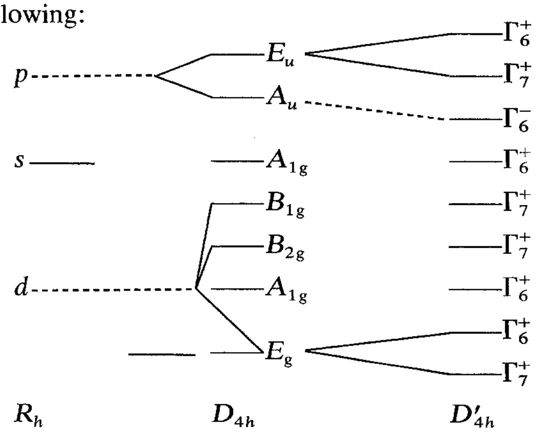
5.5. *Pseudo-Relativistic Results*

Not only is there a substantial shifting of energy levels as a consequence of the relativistic effect (see for example Figs. 6b and 7b), but, the actual symmeteries of the highest occupied orbitals are altered. In $PtCl_4^{2-}$, for example, the highest occupied orbital is B_{2g} (substantially d_{xy}) in the non-relativistic case but is Γ_6^+ (largely d_{xz}) in the relativistic treatment. Similarly, in *cis*-$Pt(NH_3)_2Cl_2$, the highest occupied non-relativistic orbital is A_1 (largely d_{z^2}) but becomes Γ_7^+ (mainly d_{xy}) relativistically. It is obvious that analagous differences occur also in the other cases presented here. While the relativistic vs. non-relativistic results may not substantially affect some of the calculated properties (i.e. nuclear quadrupole moments, total energy minima, etc.), these will be important considerations in the calculation and interpretation of electronic spectra. Further studies are currently underway to calculate electronic spectra with the inclusion of relativistic effects. However, in order to attain results that may be regarded as satisfactory, simultaneous diagonalization of both the relativistic and ligand field effects must be incorporated into the self consistent routine. The general version of our SC-MEH program does not provide the means of doing this; however, we have a more specialized version which could be employed for these purposes, but only after substantial program modification and testing has been made.

In summary, the present work not only demonstrates the adequacy of the SC-MEH in treating heavy metal complexes, but also emphasizes the practical realization of the importance of relativistic effects in the bonding of heavy metals and provides some quantitative assessment of it.

Appendix

The effect of spin-orbit coupling as found in platinum is considered in this approximation to have primarily a perturbative effect on the overall molecular orbitals and their energies. A more accurate approach wherein the MO calculation is completely diagonalized with a starting pseudo-relativistic AO basis is currently underway. Point group symmetry considerations lead to the following:



The relativistic AO basis set for d orbitals within the D'_{4h} point group may be thus constructed using the tables of Onodera and Okazaki [14]. In the following basis sets, α and β refer to the electron spins:

$$\begin{array}{lll}
d^*_{3/2}: & \Gamma_6^+ & -\sqrt{2/5}\,|0)\ \alpha+\sqrt{3/5}\,|1)\ \beta \\
 & & \sqrt{3/5}\,|-1)\alpha-\sqrt{2/5}\,|0)\ \beta \\
 & \Gamma_7^+ & \sqrt{2/5}\,|0)\ \alpha+\sqrt{1/5}\,|-1)\beta \\
 & & \sqrt{1/5}\,|1)\ \alpha-\sqrt{4/5}\,|2)\ \beta \\
d_{5/2} & \Gamma_6^+ & \sqrt{3/5}\,|0)\ \alpha+\sqrt{2/5}\,|1)\ \beta \\
 & & \sqrt{2/5}\,|-1)\alpha+\sqrt{3/5}\,|0)\ \beta \\
 & \Gamma_7^+ & \sqrt{1/5}\,|-2)\alpha+\sqrt{4/5}\,|-1)\beta \\
 & & \sqrt{4/5}\,|1)\ \alpha+\sqrt{1/5}\,|2)\ \beta \\
 & & |2)\alpha \\
 & & |-2)\beta \\
p^*_{1/2} & \Gamma_6^+ & -\sqrt{1/3}\,|0)\ \alpha+\sqrt{2/3}\,|7)\ \beta \\
 & & \sqrt{2/3}\,|-1)\alpha-\sqrt{1/3}\,|0)\ \beta \\
p_{3/2} & \Gamma_6^+ & \sqrt{2/3}\,|0)\ \alpha+\sqrt{1/3}\,|1)\ \beta \\
 & & \sqrt{1/3}\,|-1)\alpha+\sqrt{2/3}\,|0)\ \beta \\
s & \Gamma_6^+ & |-1)\beta \\
 & & |1)\alpha.
\end{array}$$

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