

## ON THE ORIGIN OF RELATIVISTIC BOND CONTRACTION

T. ZIEGLER<sup>‡</sup>, J.G. SNIJDERS and E.J. BAERENDS*Scheikundig Laboratorium, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands*

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The origin of the well-established relativistic bond contractions is investigated in the Au<sub>2</sub>, AuH and AuCl model systems. It is shown that, contrary to popular belief, this contraction is not caused by relativistic orbital contractions. Rather it has to be ascribed to a relaxation of kinetic repulsion, which is quite independent of changes in the form of the orbitals.

## 1. Introduction

The effect relativity has on bonding in compounds containing heavy elements has been the subject of several recent investigations. A variety of methods has been applied, including one-centre expansion Dirac–Fock [1], pseudopotential approaches [2,3], the Hartree–Fock–Slater method including relativity to first order [4,5] and the relativistic multiple-scattering X $\alpha$  method [6,7]. Calculations on third-row diatomics using these various methods, show that relativity in general tends to shorten the equilibrium bond length in these compounds, while the strength of the bond can both be increased or decreased depending on the system in question [8,9]. On the other hand, it has been known for some time from relativistic work on atoms, that direct relativistic effects cause s and p orbitals to contract, while the d orbitals expand somewhat due to increased shielding of the nucleus by the s and p electrons [10–13]. This circumstance has led various authors to the conclusion [5,14,15] that in s or p bonded diatomics the relativistic bond-length contraction is a consequence of the atomic orbital contraction, the reasoning being that in order to achieve efficient overlap of the contracted atomic orbitals the nuclei have to be closer to each other. This conclusion is, however, based on circumstantial evidence only, not on any actual analysis of the various relativistic corrections to the binding energy as a function of bond length.

<sup>‡</sup> Present address: Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada.

The purpose of this paper is to gain insight in the factors determining bond-length contraction by means of the perturbative Hartree–Fock–Slater (HFS) method. In a subsequent paper [16], a large class of molecules will be dealt with in more detail by this method.

## 2. Method

As our non-relativistic starting point, we take the HFS method defined by the equation

$$F^0 \phi_i^0 = \left(-\frac{1}{2} \nabla^2 + V_N + V_C + V_X\right) \phi_i^0 = \epsilon_i^0 \phi_i^0,$$

where  $V_N$ ,  $V_C$  and  $V_X$  are the nuclear, Coulomb and exchange potential, respectively. It differs from the HF equation only through Slater's approximation of the exchange  $V_X = K\rho^{1/3}$  where  $\rho$  is the total electronic density.

This equation is solved in the usual manner by expansion in a basis set of Slater-type functions, which in the sequel will be of double-zeta quality or better. For details on the method used we refer to the literature [17]. Relativistic effects are then introduced by perturbation theory to order  $\alpha^2$  in the fine-structure constant  $\alpha = e^2/4\pi\epsilon_0\hbar c$ , giving rise to the following first-order operators:

$$h_{MV} = -\frac{1}{8}\alpha^2 p^4,$$

the mass–velocity correction,

$$h_D = \frac{1}{8}\alpha^2 \nabla^2 V_T^0,$$

the Darwin correction,  $V_T^0$  being the total zeroth-order potential,

$$h_{SO} = \frac{1}{2}\alpha^2 s \cdot (\nabla V_T^0 \times p),$$

the spin-orbit correction,

$$V_T^1 = \int [\rho^1(r_1)/|r-r_1|] dr_1 + \frac{1}{3}K(\rho^0)^{-2/3}\rho^1,$$

the correction to the electronic potential;  $\rho^1$  is the first-order correction to the density

The first-order correction to the orbitals can be determined through the perturbation equation

$$(F^0 - \epsilon_i^0)\phi_i^1 = (\epsilon_i^1 - h^1)\phi_i^0,$$

while the  $\epsilon_i^1$  are determined from  $\epsilon_i^1 = \langle \phi_i^0 | h^1 | \phi_i^0 \rangle$ . Since  $h^1$  contains  $\rho^1$  and hence the  $\phi_i^1$  through the potential term  $V_T^1$  this equation has to be solved iteratively until self-consistency

For the first-order correction to the total energy one can derive:

$$E^1 = \int_{X=X'} (h_{MV} + h_D + h_{SO})\rho^0(X, X') dX.$$

Note that the  $V_T^1$  term is absent in this expression, a consequence of the stationarity of the zeroth-order energy against first-order changes in the density (for proof see ref. [16]). It should be emphasized that since  $E^1$  does not contain the  $\phi_i^1$ , it is totally independent of relativistic contractions of the orbitals. This effect enters only in the second-order correction to the total energy, for which one obtains:

$$E^2 = \frac{1}{2} \int_{X=X'} (h_{MV} + h_D + h_{SO})\rho^1(X, X') dX,$$

where  $\rho^1 = \sum_{occ} \phi_i^0 \phi_i^{1*} + c.c.$  is the factor that introduces the dependence on orbital contractions.

### 3. Results and discussion

We have applied this perturbative HFS scheme to the diatomic compounds  $Au_2$ , AuH and AuCl. The results of these calculations for the equilibrium bond lengths  $R_e$ , the dissociation energies  $D_e$  and vibrational frequencies  $\omega_e$  are presented in table 1, while the bonding energy  $\Delta E$  as a function of internuclear distance is shown in fig. 1. It is seen that in all cases relativity causes a marked contraction of bond lengths, the percentages being  $Au_2$ : 16%, AuH: 13% and AuCl: 5%. For  $Au_2$  and AuH the relativistic results compare rather well with experiment. In  $Au_2$  and AuH relativity strongly (115 and 84%) stabilizes the bond, but in AuCl weakens it slightly (9%) even though the equilibrium bond distance is still shortened. The vibration frequencies too are strongly influenced in  $Au_2$  and AuH (116 and 32%), the effect being somewhat less again in AuCl (6%). The calculated relativistic  $D_e$  and  $\omega_e$  are again seen to be in good agreement with experiment. The smallness of relativistic effects in AuCl compared to  $Au_2$  and AuH, is probably due to the fact that this compound is much more ionic than the other two, so that the valence orbitals are largely concentrated on the Cl centre, where relativistic effects are substantially smaller than on Au.

In order to gain some insight into the relativistic bond-length corrections we split the binding energy of the molecule AB with respect to atoms A and B, in a non-relativistic contribution  $\Delta E_{AB}^{nrel}$  and first- and second-order relativistic corrections  $\Delta E_{AB}^1$  and  $\Delta E_{AB}^2$

$$\Delta E_{AB}^{rel}(R) = \Delta E_{AB}^{nrel}(R) + \Delta E_{AB}^1(R) + \Delta E_{AB}^2(R),$$

where  $\Delta E_{AB}^{nrel}(R) = E_{AB}^{nrel}(R) - E_A^{nrel} - E_B^{nrel}$ , etc.

In fig. 2 we show the functions  $\Delta E_{AB}^1(R)$  and  $\Delta E_{AB}^2(R)$  for the  $Au_2$ , AuH and AuCl molecules. It is seen that in all cases  $\Delta E^2$  is a very flat function of  $R$  and hence has very little influence on the position

Table 1  
Equilibrium distances  $R_e$ , dissociation energies  $D_e$  and vibration frequencies  $\omega_e$  of some diatomic Au compounds

	$R_e(\text{\AA})$			$D_e(\text{kcal/mol})$			$\omega_e(\text{cm}^{-1})$		
	non-rel.	rel	exp	non-rel.	rel	exp	non-rel	rel	exp
$Au_2$	2.90	2.44	2.47 [18]	27	58	$52 \pm 2$ [19]	93	201	191 [18]
AuH	1.78	1.55	1.52 [14]	37	68	$74 \pm 3$ [20]	1704	2241	2305 [21]
AuCl	2.44	2.31	—	64	58	$69 \pm 15$ [22]	363	386	383 [23]

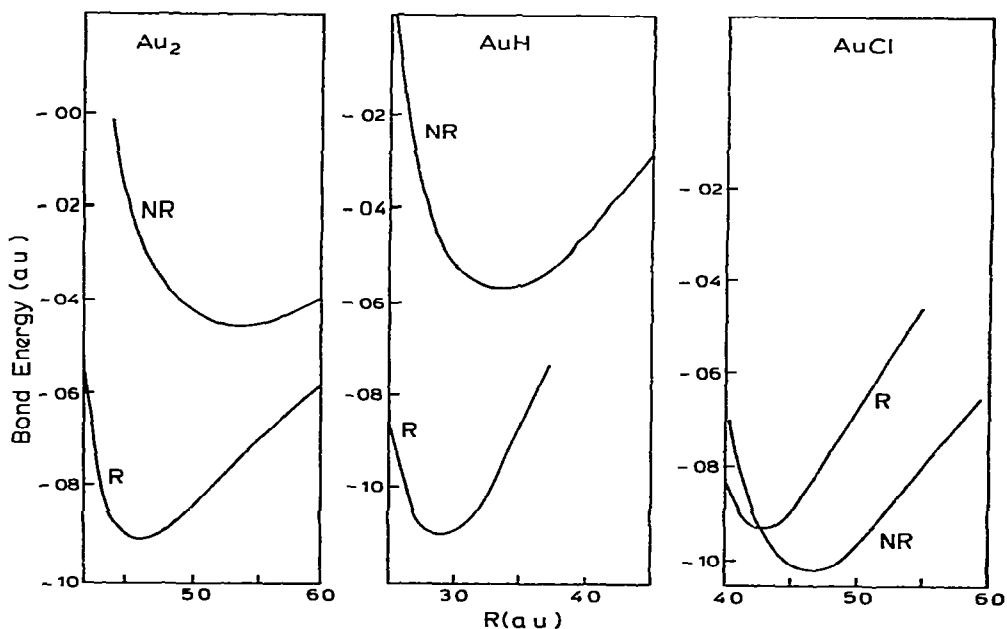


Fig 1 Relativistic (R) and non-relativistic (NR) bonding energies for Au<sub>2</sub>, AuH and AuCl as a function of internuclear distance.

of the minimum of  $\Delta E^{\text{rel}}$  i.e. the relativistic equilibrium bond length, even though its contribution to the dissociation energy is not quite negligible at least in AuH. The first-order correction  $\Delta E^1$  on the other hand

is a steeply rising function of  $R$ , and can therefore be identified as the main factor in the contraction of the bond length due to relativity. We have seen, however, in the previous section, that  $\Delta E^1$  is completely inde-

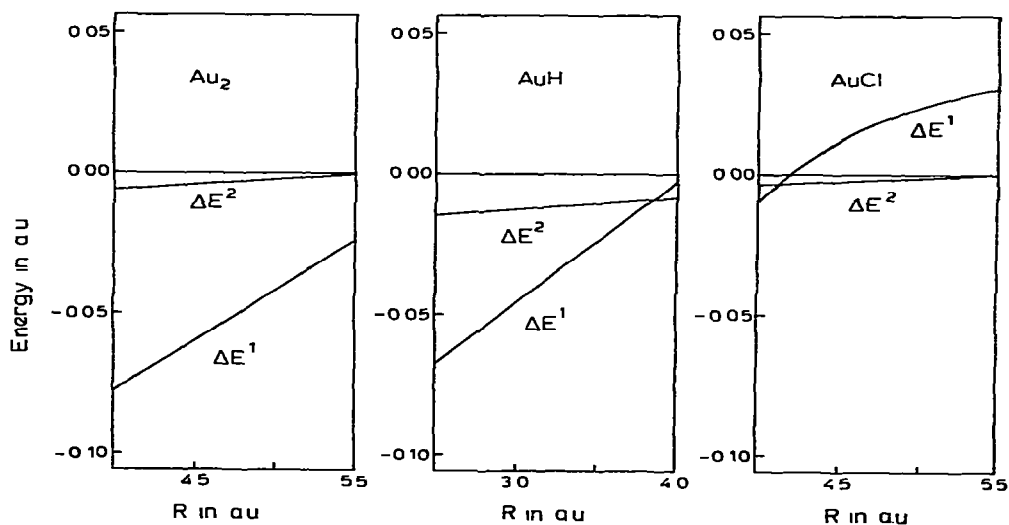


Fig 2 First- and second-order relativistic corrections to the bonding energies of Au<sub>2</sub>, AuH and AuCl as a function of internuclear distance

pendent of orbital contractions since it only involves the zeroth-order (non-relativistic) electron density  $\rho^0$ . We can therefore conclude that bond-length contractions are *not* caused by orbital contractions. Actually it is not difficult to understand the physical reason for the contraction caused by  $\Delta E^1$ . Non-relativistically the kinetic energy rises as the atoms are pushed together, in accordance with the uncertainty principle since the electrons are forced to occupy a smaller volume (of course the potential energy falls at first leading to a minimum in the energy curve). The most important contribution to  $\Delta E^1$  is the mass-velocity correction to the kinetic energy  $-\alpha^2/8p^4$ , a negative definite quantity, which will tend to become more and more negative as the positive non-relativistic kinetic energy  $\frac{1}{2}p^2$  goes up. It therefore partly relaxes the kinetic repulsion and will cause the minimum in the binding energy curve to shift to smaller internuclear distances, thus explaining the relativistic bond-length contraction. Recently the conclusions of this paper have been confirmed by an independent method by Snijders and Pyykkö [26].

<sup>1</sup> Incidentally it is possible to express the first-order change in the binding energy of a diatomic through the first-order density correction  $\rho^1$  at *all* nuclear distances  $R \geq R_c$  by means of the Hellmann-Feynman (see e.g. ref. [24]) theorem:  $\Delta E^1 = \int_{\infty}^R dR \int d\tau_1 \rho^1(R, 1) (\partial V_N / \partial R) d\tau_1$ , where  $V_N$  is the nuclear potential, the integrations are over the electronic coordinate and the internuclear distance. In our opinion, however, one should not interpret this equation as meaning that the energy change  $\Delta E^1$  is caused by the density change  $\rho^1$ . This electrostatic view of binding by virtue of the Hellmann-Feynman theorem is misleading, erroneously suggesting that the kinetic energy does not play a role in the formation of a chemical bond, as is well known non-relativistically (see e.g. ref. [25]). We thank a referee for bringing up this point.

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