

## IS THE RELATIVISTIC CONTRACTION OF BOND LENGTHS AN ORBITAL-CONTRACTION EFFECT?

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Bond lengths of AuH and TiH are calculated using numerical one-centre expansion Hartree-Fock wavefunctions, incorporating relativistic effects as a first-order perturbation. The resulting relativistic bond-length contractions thus obtained using non-relativistic wavefunctions are comparable to the full Dirac-Fock ones. This confirms that the orbital and bond-length contractions are "parallel" consequences of the mass-velocity term but that the former is not necessary for the latter.

### 1. Introduction

It is by now established that the effect of relativity on chemical bond lengths is in most cases a contraction. The first result on  $H_2^+$  was obtained in 1969 [1]. The first results on heavy molecules like  $PbH_4$  [2], AuH [3] or TiH [4] using the Dirac-Fock one-centre expansion (DF OCE) method suggested that the contraction

$$C = [R_e(nr) - R_e(rel)] / R_e(nr) \quad (1)$$

of the M-H bonds in these molecules is about 6–7%. Later, independent investigations using other methods are collected in table 1 and suggest a somewhat larger contraction for AuH and a slightly smaller one for TiH. The present situation has been summarized in refs. [5,6].

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Table 1  
Relativistic bond-lengths contractions for AuH and TiH

Molecule	$R(nr)$ (pm)	$R(rel.)$ (pm)	$R(exp)$ (pm)	Contraction		Method	Ref.
				$\Delta R$ (pm)	$C$ (%)		
AuH	174.7	162.2	152.37 <sup>a)</sup>	12.6	7.2	DF OCE	[3,5] b)
	176.3	150.8		25.5	14.5	pseudopot. HF	[8]
	182.0	151.4		30.6	16.8	pseudopot. GVB	[8]
	180.7	152.2		28.5	15.8	pseudopot. CI	[8]
	178	155		23	13	pert. HFS	[7]
	–	164		11	6	pert. HF OCE	present work
TiH	200.7	186.7	186.6 <sup>c)</sup>	13.9	6.9	DF OCE	[4,5] b)
	194	184		11	5.4	pseudopot.	[11]
	195.2	190.2		5	2.6	pseudopot.	[12]
	–	188		13	6	pert. HF OCE	present work

a) Ref. [9]. b) The original fit was replaced by a Morse-potential fit in ref. [5]. c) Ref. [10].

The bond-length contraction was commonly interpreted as a consequence of the relativistic contraction of individual s and p valence atomic orbitals (AOs). Recently, however, Ziegler et al. [7] showed using the perturbative Hartree–Fock–Slater method [13,14] that most of the contraction is obtained with the uncontracted, non-relativistic wavefunctions if the relativistic first-order terms of order  $\alpha^2$  were included in the hamiltonian. The relativistic change of the wavefunction had only a minor influence on the bond length.

Thus the contraction of orbitals and the contraction of bond lengths must be viewed as two parallel but independent consequences of the mass–velocity term, partially cancelled by the Darwin term. The same conclusion also held for several non-hydrides studied by them. The purpose of the present work is to verify their conclusion using the DF OCE program of ref. [3] and the non-relativistic wavefunctions of refs. [3,4].

## 2. Theory

In order to compare the results of a fully relativistic and a first-order perturbation approach, it is useful to treat both in a unified framework. The usual way of going over to the non-relativistic limit of the Dirac (–Fock) equation, does not only entail an expansion in powers of the fine-structure constant ( $\alpha = e^2/4\pi\epsilon_0\hbar c = 7.29735 \times 10^{-3}$ ) but also a concurrent change of picture, decoupling the upper and lower two components of the four-spinors to the required order, the well-known Foldy–Wouthuysen (FW) transformation. This unitary transformation of the hamiltonian and its eigenstates is given to first order by

$$U = \exp(\beta\boldsymbol{\alpha}\cdot\mathbf{p}/2mc) \simeq 1 + \beta\boldsymbol{\alpha}\cdot\mathbf{p}/2mc, \quad U^\dagger \simeq 1 - \beta\boldsymbol{\alpha}\cdot\mathbf{p}/2mc. \quad (2)$$

The non-relativistic approximation to the eigenstates can then be written as

$$\psi'_{\text{rel}} = \begin{pmatrix} \phi \\ 0 \end{pmatrix}, \quad (3)$$

where the two-component  $\phi$  is a solution to the non-relativistic Schrodinger or Hartree–Fock equation and the two lower components vanish for positive energy solutions and are usually dropped. For our purposes it is convenient, however, to consider the non-relativistic approximation in the original Dirac picture, which is easily found by back transforming  $\psi'_{\text{rel}}$  with the FW transformation (2)

$$\psi_{\text{rel}} = U^\dagger \psi'_{\text{rel}} = (1 - \beta\boldsymbol{\alpha}\cdot\mathbf{p}/2mc) \begin{pmatrix} \phi \\ 0 \end{pmatrix} = \begin{pmatrix} \phi \\ (\boldsymbol{\sigma}\cdot\mathbf{p}/2mc)\phi \end{pmatrix} \quad (4)$$

in the Dirac picture.

It should be emphasized that this four-component  $\psi_{\text{rel}}$  is still completely non-relativistic, differing from  $\psi'_{\text{rel}}$  merely by a change of picture which does not effect any of the physics involved [15], in particular  $\psi_{\text{rel}}$  does not contain any of the orbital contractions present in fully relativistic eigenfunctions. There is a slight difference of meaning between the position operators in the two pictures (see e.g. ref. [16]), but since it only becomes apparent in domains of the order  $\hbar/mc \approx 0.007$  bohr, being two orders of magnitude smaller than a typical orbital contraction, it thus does not affect our argument and need not concern us here. To find the first-order corrections to the eigenvalues of the Dirac hamiltonian we can now just calculate the expectation value of this hamiltonian with respect to  $\psi_{\text{rel}} = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$ . Assuming  $\phi$  to be normalized we obtain

$$\begin{aligned} \epsilon_i &= \frac{\langle \psi_{\text{rel}} | h_D | \psi_{\text{rel}} \rangle}{\langle \psi | \psi \rangle} = \frac{1}{2m} \frac{\langle \psi | c\boldsymbol{\sigma}\cdot\mathbf{p} | \chi \rangle + \text{c.c.} - 2mc^2 \langle \chi | \chi \rangle + \langle \phi | V | \phi \rangle + \langle \chi | V | \chi \rangle}{1 + \langle \chi | \chi \rangle} \\ &= \epsilon_i^{\text{rel}} - (1/4m^2c^2)\epsilon_i^{\text{rel}} \langle \phi | p^2 | \phi \rangle + (1/4m^2c^2)\langle \phi | (\boldsymbol{\sigma}\cdot\mathbf{p}) V (\boldsymbol{\sigma}\cdot\mathbf{p}) | \phi \rangle. \end{aligned} \quad (5)$$

After some algebra using

$$\langle \phi | V p^2 | \phi \rangle = \epsilon_i^{\text{nrrel}} \langle \phi | p^2 | \phi \rangle - (1/2m) \langle \phi | p^4 | \phi \rangle, \quad (6)$$

since  $\phi$  is a solution to the non-relativistic equation, we find

$$\epsilon_i = \epsilon_i^{\text{nrrel}} - (1/8m^3 c^2) \langle \phi | p^4 | \phi \rangle + (\hbar^2/8m^2 c^2) \langle \phi | (\nabla^2 V) | \phi \rangle + (\hbar/4m^2 c^2) \langle \phi | \boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}) | \phi \rangle \quad (7)$$

to the relevant order. In the Dirac–Fock case some additional potential terms arise, due to the dependence of  $V$  on the orbitals, that are not relevant here [13].

This result, containing the usual mass–velocity, Darwin and spin–orbit terms, is of course identical to that obtained by perturbation theory in the FW transformed picture, showing explicitly the equivalence of the two pictures.

In a similar way, the first-order relativistic correction to the total energy can be calculated using the non-relativistic orbital  $\psi_i^{\text{nrrel}}$ . This first-order total energy does not contain the effect of orbital contractions, which only appears in higher orders due to corrections to  $\psi_{\text{nrrel}}$ . In the DF OCE program the non-relativistic orbitals are generated by using a very high velocity of light ( $c' = 10^{10}$  au), and are hence obtained in the form

$$\psi'' = \begin{pmatrix} \phi \\ (\boldsymbol{\sigma} \cdot \mathbf{p} / 2mc') \phi \end{pmatrix}.$$

To get the non-relativistic orbitals in the Dirac ( $c = 137.037$ ) picture, we can just multiply the lower component by the ratio  $c'/c$  and renormalize. The first-order total energy is then calculated by executing the DF OCE program [3] with these orbitals without further iterations and using the actual velocity of light. Running the program to self-consistency then of course gives us the fully relativistic energies, which have already been calculated for the systems treated below [3,4].

### 3. Results

The calculated potential energy curves for TIH are shown in fig. 1. The present, perturbative Hartree–Fock OCE values for  $R_e$  are included in table 1. The total energies are shown in table 2. Most of the relativistic energy lowering arises, of course, from the deep core. The present method retrieves 79.9 and 78.9% of the relativistic energy lowering for AuH and TIH, respectively.

As far as the relativistic bond-length contraction is concerned, the present method gives about 90% of the differ-

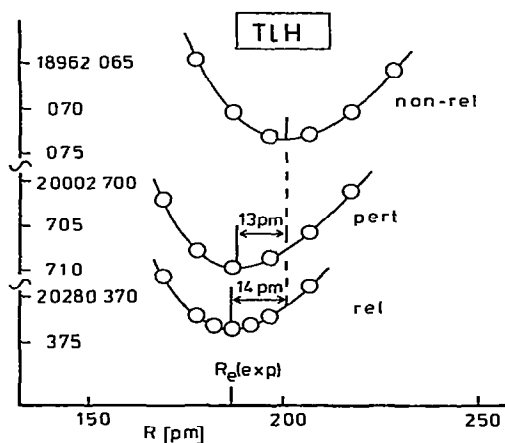


Fig. 1. The calculated non-relativistic (HF OCE), relativistic (DF OCE) and the present perturbation HF OCE potential energy curves for the TIH molecule. The curves are the fitted Morse potentials.

Table 2  
Calculated total energies,  $E_T$ , for AuH and TiH

Molecule	$-E_T$ (au)		
	HF OCE	Pert. HF OCE	DF OCE
AuH	17865 714	18804.576	19040.175
TiH	18962 073	20002.710	20280.374

ence between HF OCE and the full DF OCE, thus showing that the bulk of the bond-length contraction is indeed obtained by using non-relativistic wavefunctions if the relativistic corrections are included as first-order perturbations. For AuH the OCE value of the contraction is itself only about half of that obtained by the two other methods, perhaps because the hydrogen atom is described by mixing in an unrealistically large amount of a gold 6p function, contracting much less than the gold 6s function. For TiH, Lee et al. [11] allow a trend towards "p<sub>1/2</sub> bonding" [4] and find a contraction, comparable to ours. Pelissier and Barthelat [12] fix the ratio of the norms  $N(6p_{3/2})/N(6p_{1/2})$  to its non-relativistic value and obtain, probably for this reason, a much smaller bond-length contraction.

#### 4. Conclusion

We have shown that most of the relativistic bond-length contraction can be obtained for AuH and TiH using the non-relativistic uncontracted orbitals, if the terms corresponding to a first-order treatment of relativistic effects are added. This fully agrees with the conclusion drawn by Ziegler et al. [7] viz.. that the answer to the title question is: no.

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