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## Relativistic Effects on Orbital Energies in AgH and AuH; A Clue to the Origin of Relativistic Correlation Effects

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Orbital energies for AuH and AgH are calculated by an all-electron relativistic self-consistent-field method using Slater type basis functions. Major relativistic effects for AgH are spin-orbit splittings and those for AuH are large shifts in orbital energies in addition to spin-orbit splittings. Relativistic effects on orbital energies in AgH and AuH imply that changes in correlation energies for relativistic calculations of AuH will be significantly larger than those of AgH, providing partial explanation for the large discrepancies in equilibrium bond length and the dissociation energy between experiments and theoretical estimates for AuH. Large relativistic effects on orbital energies indicate that relativistic contributions should be included for the correct interpretation of ionization potentials for these molecules. Relativistic effects are also evident in dipole moments for these molecules.

### Introduction

Diatomic molecules AgH and AuH are quite interesting molecules from the computational point of view, exhibiting very large relativistic and correlation effects on bond lengths and dissociation energies as shown by the previous studies<sup>1,2</sup>. When the relativistic effects estimated from Dirac-Hartree-Fock (DHF) calculations using analytic expansions, which is referred as the all-electron relativistic self-consistent-field (RSCF) calculations, and the correlation effects from non-relativistic calculations are combined<sup>3</sup>, the equilibrium bond length and the dissociation energy for AgH from the calculations are in good agreement with experimental values whereas those for AuH are not. It is evident that the correlation effects caused by the shift of energy levels and the change of orbital shapes due to the relativistic effects play an important role for the correct description of the electronic structure of AuH.

In order to understand the synergistic effect between correlation and relativity, both of them should be treated simultaneously in one calculation using a correlated method based upon a relativistic formalism. Although this procedure for all-electron calculations is not difficult to conceptualize and a formalism has been reported<sup>4</sup>, the actual calculations even for small molecules are not available. The majority of calculations which include both the relativistic and correlation effects are based upon effective core potentials with only the minimum amount of valence correlations required for the qualitatively correct description of several valence state potential curves<sup>5,6</sup>.

Since all-electron calculations including both the relativistic and the correlation effects are not readily available at present, we try to find a clue to the source of relativistic correlation effects, the extra correlation effects caused by the introduction of relativistic effects, for AuH from the result of previous RSCF calculations for AgH and AuH.

Properties mainly analysed here are the orbital energies of relevant molecules and atoms obtained from relativistic (RSCF) and nonrelativistic self-consistent field (NRSCF) calculations. The orbital energies for AgH and AuH are also useful in understanding the bonding properties of these molecules and could be very helpful in interpreting photoelectron spectra of these molecules when the experimental results become available.

In the next section, calculations employed for the present study is briefly sketched with discussions about the quality of basis functions used. In recent years, many theoretical studies have been performed about the basis set requirement in RSCF calculations indicating that the kinetic balance is a crucial factor<sup>7-10</sup>. In terms of the kinetic balance, the basis sets for AgH and AuH are not completely balanced because of the computational reasons, but the basis sets are adequate for molecular properties discussed here as will be shown in the next section. The result of RSCF calculations for small molecules and atoms are also available<sup>11</sup>. We have performed RSCF calculations using basis sets satisfying the kinetic balance condition<sup>11</sup>. The following section contains selections from the calculated values and discussions about their implication to correlation energies.

### Calculations

All-electron relativistic SCF calculations for AuH and AgH

have been performed using a RSCF program for linear molecules, which is a DHF program based upon analytic expansions. The details of calculations and the formalism are available in our previous report<sup>2</sup> for these molecules and only a few points about the method and basis sets are mentioned here for the clarity of presentation.

The Hamiltonian used in the present relativistic calculations is similar to that used in the numerical DHF calculations for atoms and contains the Dirac operator for one-electron term and the conventional electron repulsion term for two-electron interactions. The wave function for the whole system is approximated by a Slater determinant for a closed-shell configuration. Because of the property of the Dirac operator, the Slater determinant is generated as a linear combination of products of four component molecular spinors (MS) approximated by expansions of basis spinors (BS). Basis spinors used in the present method are also four component functions, but only one of the four components is allowed to be a non-zero function represented by Slater type function (STF) with an integer power of radius  $r$ . It is noted that the use of STF's with integer powers of  $r$  does not satisfy cusp conditions for atomic spinors (AS) and should be viewed as an additional approximation.

Four components of the spinors can be separated into two groups, two large and two small components, according to their magnitudes in general situations. The large components correspond to two component representations of the major por-

**Table 1. Total and Orbital/Spinor Energies (in a.u.) from Au<sup>+</sup> Calculations. The Quantum Numbers  $j$  for Atomic Spinors are in parentheses**

Spinors (orbitals)	Relativistic			Nonrelativistic	
	RSCF(C) <sup>a</sup>	DHF <sup>b</sup>	RSCF(10 <sup>9</sup> ) <sup>c</sup>	NRSCF <sup>d</sup>	NRSCF(TZV) <sup>e</sup>
1s(1/2)	-2984.03	-2988.16	-2706.84	-2706.96	-2707.11
2s(1/2)	-532.75	-532.75	-456.80	-456.39	-457.46
3s(1/2)	-128.37	-128.46	-109.13	-109.16	-109.54
4s(1/2)	-29.264	-29.461	-24.526	-24.483	-24.630
5s(1/2)	-4.903	-4.995	-4.033	-4.027	-4.086
2p(3/2)	-441.89	-442.00	-439.05	-439.15	-439.19
(1/2)	-506.42	-509.09	-439.77		
3p(3/2)	-102.82	-103.04	-100.74	-100.82	-100.90
(1/2)	-117.21	-118.157	-101.06		
4p(3/2)	-21.206	-21.375	-20.746	-20.765	-20.848
(1/2)	-24.621	-25.047	-20.797		
5p(3/2)	-2.813	-2.873	-2.770	-2.770	-2.815
(1/2)	-3.383	-3.502	-2.776		
3d(5/2)	-82.806	-83.044	-84.856	-84.933	-84.998
(3/2)	-85.981	-86.362	-84.863		
4d(5/2)	-13.309	-13.480	-13.837	-13.855	-13.933
(3/2)	-13.995	-14.174	-13.841		
5d(5/2)	-0.694	-0.740	-0.763	-0.767	-0.801
(3/2)	-0.754	-0.805	-0.762		
4f(7/2)	-3.807	-4.029	-4.449	-4.494	-4.605
(5/2)	-3.952	-4.176	-4.454		
E(Total)	-19022.25	-19039.55	-17865.52	-17862.54	-17865.16

<sup>a</sup> All-electron relativistic SCF calculations with the basis set of Ref. 2. <sup>b</sup> Numerical atomic DHF calculations. <sup>c</sup> Same as a, but the value for the speed of light is set as 10<sup>9</sup> a.u. <sup>d</sup> Nonrelativistic SCF calculations using the large component basis set of a and c. <sup>e</sup> Nonrelativistic SCF calculations with large basis set. Triple zeta quality for outer most orbitals of each  $l$  value.

tion of electron densities and closely related to the orbitals in the conventional nonrelativistic calculations. In this view, the small components are the auxiliary functions to large components which are necessary to produce kinetic energies from the momentum operator and other relativistic contributions<sup>2,8</sup>. Therefore, the quality of basis set in the ordinary sense used in the electronic structure calculations is determined by that of large component and the basis set quality for small components should be analysed in a different context.

The list of basis sets for Au, Ag and H are given in the earlier report<sup>2</sup> of the work along with the explanation for the considerations that lead to these particular selections. The basis sets for large components are double zeta quality for Au and better than double zeta qualities for Ag and H atoms. There are 6p functions for Au and 5p functions for Ag in the basis sets, but no polarization functions are provided for d shells. Instead of including all the derivative functions of the large component basis functions in the small component basis as required by the kinetic balance condition between large and small components, the present selection of small component basis set is the result of compromise between the theoretically important kinetic balance and the computational considerations. The partial kinetic balance for the present basis set is adequate enough for the reliable description of many molecular properties treated here as will be discussed later in this report.

In our calculations, STF's with  $n=1$ , i.e. 1p, 2d and 3f etc., are only allowed to the small component basis and not permitted in the large component basis although they are part of both the large and small components in the exact eigenfunctions of hydrogen-like atoms. These functions produce spurious roots which make convergence of the SCF procedure very difficult, if not impossible. This point is discussed elsewhere in more detail<sup>2,11</sup>.

Since our present RSCF program can handle only atoms and diatomic molecules with a closed-shell configuration, we also utilize the numerical atomic DHF calculations and nonrelativistic calculations whenever appropriate.

In order to show the quality of our RSCF calculations, we summarize the energies and orbital energies for Au\* from several different wave functions in Table 1. We present our results at this level of details in order to clarify the approximate nature of our RSCF basis functions in terms of the completeness of the large component space as well as in terms of kinetic balance.

The total energies of Au\* from various calculations in Table 1 display large differences indicating that the double zeta basis set is far from the basis set limit and the kinetic balance is not perfect. The error due to the imperfect kinetic balance is mainly responsible for the differences between RSCF(10<sup>5</sup>) and NRSCF energies, which is about 3 a.u.. Since the correct nonrelativistic limit is obtained only when the speed of light becomes infinite in the RSCF calculations, the finite value of 10<sup>5</sup> for the speed of light also contribute to lower the energy of RSCF calculations by a little amount. The imperfectness of the kinetic balance and the finite value for the nonrelativistic speed of light are also reflected in the small spin-orbit splittings in RSCF orbitals, but the splittings are small enough to be neglected for most purposes.

We feel that the kinetic balance for the present basis set is quite adequate as can be seen from the good agreement between orbital energies of Au\* from RSCF calculations with  $c=10^5$  and those from NRSCF calculations with the large com-

ponent basis set. From the differences between two NRSCF results with different basis sets, we may assume that the major source of the discrepancies between RSCF calculations and DHF calculations are the basis set deficiency in double zeta quality large component basis set. The largest error in orbital energies in Table 1 is about 6 percent, but the error in splittings is quite small and all orderings of the spinor energies are correct. Therefore, we expect that molecular properties from the present calculations are quite reasonable.

## Results and Discussions

Orbital energies of AgH from several calculations at  $R=3.2$  a.u., which is close to equilibrium bond lengths from RSCF (3.2 a.u.) and NRSCF (3.3 a.u.) calculations, are summarized in Table 2. Orbital energies for RSCF calculations with  $c=10^5$  are quite close to those from NRSCF calculations with the same basis set and also to those from better basis set, NRSCF (NC) in Table 2. Here again, the spin-orbit splittings in RSCF calculations reflect quality of small component basis functions for these calculations from the view point of kinetic balance. The fact that these splittings are quite small, less than 0.001 a.u., for outer orbitals in RSCF calculations with  $c=10^5$  in Table 2, indicate that the kinetic balance is more complete in Ag basis set than in Au.

When the orbital energies of RSCF calculation are compared with those of corresponding nonrelativistic calculations, RSCF with  $c=10^5$  of NRSCF, the major relativistic effects are spin-orbit splittings in Table 2. Although the spin-orbit effects are quite large for inner orbitals, they are only about 0.04 a.u. for orbitals composed of 4d orbitals. This may be

**Table 2. Total and Orbital/Spinor Energies (in a.u.) and Dipole Moments for AgH. All the Values are for  $R=3.2$  a.u. and Orbital Energies for Inner Core Orbitals are Omitted from the Table. Orbitals are Designated in  $\omega-\omega$  Coupling Symmetry Labels and Major Atomic Components of Ag are Given in Parentheses**

	RSCF(c) <sup>a</sup>	RSCF(10 <sup>5</sup> ) <sup>b</sup>	NRSCF <sup>c</sup>	NRSCF(NC) <sup>d</sup>
1/2 spinors or orbitals				
(5s)	-0.318	-0.308	-0.306	-0.312
(4d)	-0.543	-0.556	-0.552	-0.553
(4d)	-0.513	-0.540		
(4p)	-2.686	-2.681	-2.674	-2.671
(4p)	-2.883	-2.690		
(4s)	-4.278	-4.009	-3.998	-3.997
3/2 spinors or orbitals				
(4d)	-0.504	-0.538	-0.534	-0.534
(4d)	-0.530	-0.541		
(4p)	-2.684	-2.680	-2.671	-2.674
5/2 spinors or orbitals				
(4d)	-0.503	-0.538	-0.534	-0.534
E(total)	-5314.475	-5198.320	-5198.223	-5198.227
Dipole(a.u.)	1.828	2.002	2.041	1.933

<sup>a</sup> All-electron RSCF calculations with the basis set of Ref. 2. <sup>b</sup> Same as a, but  $C=10^5$  corresponds to nonrelativistic limit. <sup>c</sup> Nonrelativistic SCF calculations using the large component basis set of a and b. <sup>d</sup> Nonrelativistic SCF calculations with more basis functions for valence shells.

**Table 3. Total and Orbital/Spinor Energies (in a.u.) and Dipole Moments (in a.u.) for AuH. Orbital Energies for Inner Core Orbitals are Omitted. Spinors are Designated in  $\omega$ - $\omega$  Coupling Symmetry Labels and Major Atomic Components of Au are Given in Parentheses**

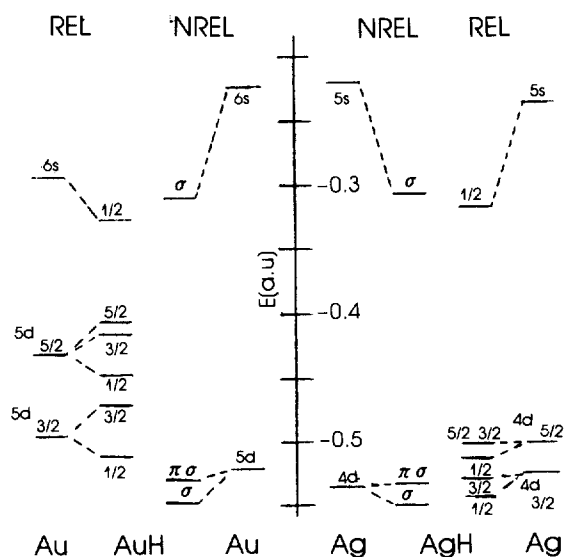
	R'=3.1 a.u.		R=3.4 a.u.		
	RSCF(C) <sup>a</sup>	RSCF(10 <sup>5</sup> ) <sup>b</sup>	RSCF(10 <sup>5</sup> ) <sup>b</sup>	NRSCF <sup>c</sup>	NRSCF(TZY) <sup>d</sup>
3/2 spinors or orbitals					
(6s)	-0.325	-0.292	-0.291	-0.290	-0.312
(5d)	-0.513	-0.553	-0.512	-0.516	-0.548
(5d)	-0.447	-0.495	-0.490		
(5p)	-2.538	-2.500	-2.496	-2.498	-2.543
(5p)	-3.110	-2.509	-2.502		
(4f)	-3.544	-4.181	-4.175	-4.219	-4.334
(4f)	-3.689	-4.181	-4.180		
(5s)	-4.638	-3.768	-3.763	-3.757	-3.817
3/2 spinors or orbitals					
(5d)	-0.416	-0.495	-0.490	-0.494	-0.528
(5d)	-0.470	-0.489	-0.488		
(5p)	-2.530	-2.497	-2.494	-2.495	-2.541
(4f)	-3.543	-4.181	-4.176	-4.219	-4.334
(4f)	-3.687	-4.186	-4.181		
5/2 spinors or orbitals					
(5d)	-0.404	-0.489	-0.488	-0.493	-0.528
(4f)	-3.542	-4.181	-4.176	-4.220	-4.335
(4f)	-3.686	-4.187	-4.183		
1/2 spinors or orbitals					
(4f)	-3.541	-4.182	-4.178	-4.222	-4.337
E(total)	-19023.066	-17866.252	-17866.259	-17863.283	-17865.920
Dipole	1.123	1.916	2.103	2.132	1.915

<sup>a,b,c</sup> Same as those in Table 2. <sup>d</sup> Nonrelativistic SCF calculations with triple zeta basis for valence shells.

large enough to be observed in experiment but relatively insignificant to affect the property of AgH in the ground state. Relativistic energy shift for a given orbital is also evident but fairly small in Table 2. It appears that dipole moments are more affected by relativistic effects than orbital energies for valence shells as shown in Table 2 implying that the orbital shapes are sensitive to relativistic effects<sup>12</sup>.

Orbital energies for AuH at internuclear distances near equilibrium bond lengths from RSCF (3.1 a.u.) and NRSCF (3.4 a.u.) are displayed in Table 3 for various SCF calculations. The quality of basis set for Au is not as good as that for Ag. This can be seen by comparing many nonrelativistic calculations, RSCF with  $c=10^5$  and NRSCF's in Table 3, or can be inferred from Au<sup>+</sup> results given in the previous section.

Orbital energy differences are significantly larger than those for AgH indicating much larger relativistic effects for AuH. Orbital (or spinor) energies of molecular spinors composed largely of 5d orbitals and of 4f orbitals are slightly higher in RSCF than those in nonrelativistic cases while orbital energies of s and p containing MS's are lowered by relativistic effects. The combined effects are large enough to make reasonable assignments of orbital energies very difficult from calculations without relativistic effects. The results of RSCF calculations for AuH, and also those for AgH to somewhat less extent, clearly demonstrate the importance of relativistic effects when the ordering of orbital energies is the property



**Figure 1.** Orbital (spinor) energies for valence orbitals (spinors) in Ag, Au, AgH and AuH from relativistic and nonrelativistic SCF calculations. Dotted lines display relations between atomic and molecular orbitals (spinors). No attempt is made to correlate nonrelativistic orbitals with relativistic spinors, but relations can be inferred from symmetry labels.

of interest as in the case of interpreting photoelectron spectra, Unfortunately, photoelectron spectra for AgH and AuH are, to the best of our knowledge, not available.

Most interesting relativistic effects for AuH are very large relativistic correlation effects in bond length and dissociation energies<sup>1-3</sup> as mentioned in the introduction while these relativistic correlation effects are almost negligible in AgH. We believe that orbital energies offer a reasonable explanation for this phenomenon. Orbital energies from relativistic and nonrelativistic SCF calculations for AgH, AuH, Ag and Au are collected in Figure 1 for s and d valence orbitals. In Figure 1, relativistic values for molecules are from RSCF calculations and nonrelativistic values for molecules are from the best NRSCF calculations available while atomic values are from DHF and HF calculations.

At a glance, the nonrelativistic Ag and AgH are quite similar to nonrelativistic Au and AuH, respectively; the conclusion of nonrelativistic studies on these molecules by McLean<sup>3</sup>, which also show that nonrelativistic correlation effects are almost same for AuH and AgH. In addition, relativistic orbital energies for AgH differ by less than 10% from nonrelativistic ones in Fig. 1 and also in Table 2. We will try to explain large relativistic correlation effects on AuH using these informations based upon perturbational point of view.

In the most popular form of the many body perturbation theory, the second order correlation energies for a HF reference state is given by

$$\Delta E(2) = \sum_{\substack{i>j \\ a>b}} \frac{\langle \Phi_{ij}^{ab} | H | \Phi_0 \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (1)$$

where  $\Phi_{ij}^{ab}$  denotes a doubly excited configuration relative to the reference state  $\Phi_0$  and denominator is given in terms of orbital energies. Since the actual values of matrix elements in numerator of Eq.(1) are not available, we assume that they are same for corresponding relativistic and nonrelativistic calculations of the same state for the reason of simplicity. Then we can estimate some trends from orbital energies alone.

Comparing various species in Figure 1, we may expect the followings from the value of denominators provided that orbital energies of given excited orbitals are similar in each system.

(1) Correlation effects on AgH are similar for NRSCF and RSCF orbitals except for small spin-orbit splittings and energy shifts. Correlation contributions are slightly larger for relativistic cases.

(2) Correlation effects for nonrelativistic Au and AuH are similar to those for Ag and AgH, respectively. Correlation effects for relativistic Au and AuH are larger than those for nonrelativistic Au and AuH. Since there are more spread in AuH than in Au for d orbitals in Figure 1, correlation effects are larger for molecules than for atoms and the same may be assumed for relativistic correlation effects, which we define as the difference between correlation energies obtainable from relativistic and nonrelativistic calculations.

It is noted here that both the upward shift of the orbital

energy and the spin-orbit splitting of an orbital, which does not shift the weighted average orbital energy, increase second order correlation energies when all the assumptions made here are valid. Therefore it is clear that relativistic contributions are much larger for correlation energies in AuH than in AgH from the simple picture of orbital energies. The bond length dependence of correlation energies are not easy to estimate from this simple argument since the orbital energy changes with internuclear distances are rather small near the equilibrium. Considering correlation contribution from other orbitals not shown in Figure 1 also favors larger correlation energies for relativistic molecules than nonrelativistic ones and larger correlation energy increase for AuH than AgH.

The exact account of correlation energies should be obtained from correlated relativistic calculations, but the importance of correlating d orbitals for correct molecular properties appears to be quite general. The main contributions from d orbitals are from spin-orbit splittings and better coupling of d orbitals with s orbitals in relativistic picture.

There are no reason to believe that correlated relativistic calculation can be performed exactly the same way as the nonrelativistic ones considering many theoretical difficulties apparent even at RSCF level. We expect that computational, if not theoretical, solutions could be found for most problems and the work in this direction is in progress. Since relativistic effects of AuH are substantial, we believe that arguments in this paper will be supported by more elaborate calculations in the future.

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