

The accuracy of the pseudopotential approximation. III. A comparison between pseudopotential and all-electron methods for Au and AuH

Peter Schwerdtfeger,^{a)} J. Reuben Brown, and Jon K. Laerdahl

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Hermann Stoll

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

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The quality of the pseudopotential approximation has been tested thoroughly by calculating spectroscopic properties of the gold atom and ground state AuH for eight different effective core potentials using Hartree–Fock, second-order Møller–Plesset and coupled cluster methods. The pseudopotential valence basis set $\{\varphi\}_v$ for Au was chosen to be identical for all pseudopotentials, a subset of the all-electron basis set $\{\varphi\}_{AE}$, and the condition was applied that all sets are of near basis set limit quality. The pseudopotential results are compared with data obtained from nonrelativistic, scalar relativistic Douglas–Kroll and fully relativistic four-component all-electron calculations. The variation between the results obtained for all valence electron small-core pseudopotentials and all electron Douglas–Kroll calculations is found to be small (for the Stuttgart pseudopotential $\Delta r_e = 0.001 \text{ \AA}$, $\Delta D_e = 0.03 \text{ eV}$, $\Delta \omega_e = 9 \text{ cm}^{-1}$, $\Delta \mu_e = 0.04 \text{ D}$). Sizable differences to all electron results are only found for the 11 valence electron large-core pseudopotentials. The effects of the basis set superposition error on spectroscopic constants were investigated. Calculated coupled cluster electron affinities and ionization potentials for gold and spectroscopic properties for AuH were found to be in excellent agreement with available experimental data. The variation between the different small-core pseudopotentials for one particular spectroscopic property is shown to be less than the error due to the incompleteness of electron correlation procedure or the basis set and approximately of the same size as the basis set superposition error. The results show that scalar relativistic effects for valence properties are perfectly described by the pseudopotential approximation. © 2000 American Institute of Physics. [S0021-9606(00)30741-3]

I. INTRODUCTION

In the two previous papers in this series^{1,2} the effects of the design of pseudopotentials on their performance, when compared with experimental data, has been examined in detail for the *p*-block element indium. The conclusions of these studies were that a large valence region (and hence small-core pseudopotential) was desirable for the accurate determination of molecular properties. Other studies have come to the conclusion that the errors in pseudopotentials can be less than negligible.^{3–5} As a result the performance of the commonly used pseudopotentials still remains somewhat uncertain, and as there are a number of research groups producing new pseudopotentials by a variety of different fitting techniques an investigation of the performance of the most commonly used pseudopotentials was felt necessary. To our opinion, however, whenever calculations revealed “serious flaws” in the pseudopotential approximation a number of important issues were disregarded. For example, large-core pseudopotentials which are well known to be not sufficiently accurate were used;¹ the pseudopotential fitting procedure was not accurate enough (e.g., the number of reference states chosen);^{6,7} scalar relativistic results were compared with

fully relativistic calculations; basis sets used in the comparison were not of similar size (this is the most common error, see for example, Ref. 5); errors have been made in the all-electron calculations as is the case in Ref. 3; or nonlinear core corrections⁸ were neglected when applying density functional theory (DFT) based pseudopotentials.

It is now well known that relativistic effects are important in heavy element containing compounds.^{9,10} The most widely used quantum chemical methods in heavy element chemistry is the pseudopotential approximation because it avoids the basis functions necessary for a description of the electronic core and for the inner nodal structure of the valence orbitals. Reviews on the application of pseudopotentials in heavy element chemistry have recently been given by Frenking *et al.*¹¹ and Pyykkö and Stoll.¹²

Since relativistic operators act in the near vicinity of the nucleus where the pseudoorbitals exhibit the wrong nodal behavior, one may raise the question if relativistic effects can be described correctly within the pseudopotential approximation. However, it has been pointed out that relativistic perturbation operators have to be replaced by valence pseudooperators which correctly describe the relativistic effects in the valence space.^{1,13,14} Such operators also have the advantage that they can be represented by simple linear combinations of Gaussian or exponential functions thus leading to one-electron integrals which are easily implemented in current *ab*

^{a)} Author to whom correspondence should be addressed. Electronic mail: schwerd@ccu1.auckland.ac.nz

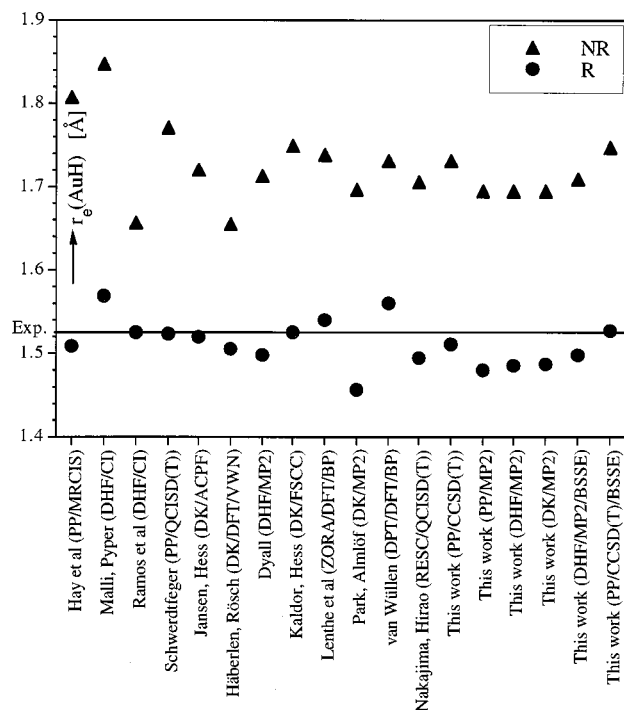


FIG. 1. A comparison of calculated AuH bond distances at the nonrelativistic and relativistic level of theory using a variety of different approximations (Refs. 15 and 16). The data are ordered according to their data of publication. Only correlated *ab initio* or density functional calculations are listed. Experimental value from Ref. 17. Abbreviations used: PP, pseudopotential; MRCIS, multireference with a subsequent configuration interaction (CI) using single excitations only; DHF, Dirac–Hartree–Fock; QCISD, quadratic configuration interaction; DK, Douglas–Kroll; ACPF, averaged coupled-pair functional; DFT, density functional theory; VWN, Vosko–Wilk–Nusair parametrization; MP2, Møller–Plesset second-order; BP, Becke–Perdew parametrization; RESC, relativistic scheme by eliminating the small component; DPT, direct perturbation theory; CCSD(T), coupled cluster singles doubles treating the triples perturbatively; BSSE, counterpoise correction for the basis set superposition error.

initio or density functional program codes. Figure 1 shows previous correlated nonrelativistic and relativistic calculations for the bond distance of AuH.^{15,16} Whilst the relativistic values are close to the experimental bond distance of AuH ($r_e = 1.524$ Å),¹⁷ there seems to be a larger uncertainty for the bond distance at the nonrelativistic level (!).

In our previous work we discussed the importance of choosing the correct size of the core for the pseudopotential approximation.^{1,2} In this paper we investigate the reliability of the relativistic approach to pseudopotentials for Au and AuH. We chose gold because scalar relativistic effects are extremely large (leading to the so-called gold maximum in the period from Cs to Rn),⁹ and spin–orbit effects for gold molecules in the electronic ground state are very small and can safely be neglected.^{18,19} We mention that there are numerous other studies on AuH,^{19,20} see for example Fig. 1. In a subsequent paper in this series we will investigate the accuracy of spin–orbit coupled pseudopotentials in detail.²¹

In the following section we briefly review some general features of the effective core potential approximation. This was felt necessary considering our discussion of the various pseudopotentials used in this paper, but also because of the current misunderstandings of this method. In Sec. III we

present the computational details and in Sec. IV we present and discuss our calculated results for Au and AuH. A conclusion is given in the last section.

II. THE EFFECTIVE CORE POTENTIAL APPROXIMATION

It is very convenient to introduce effective core potentials (ECP) by replacing the all-electron Hamiltonian of the system with a valence electron model Hamiltonian H_v for n_v valence electrons and N_c cores (nuclei),

$$H_v = -\frac{1}{2} \sum_i^{n_v} \nabla_i^2 + \sum_{i < j}^{n_v} \frac{1}{r_{ij}} + \sum_i^{n_v} \sum_a^{N_c} V_{CV}^a(r_{ai}) + \sum_{a < b}^{N_c} V_{CC}^{ab}(r_{ab}), \quad (1)$$

where V_{CV} and V_{CC} are the corresponding ECPs for the core–valence and core–core interactions, respectively. Strictly speaking, the Hamiltonian *cannot* be separated into a core, valence, and mixed core–valence Hamiltonian because electrons are indistinguishable. ECPs are therefore introduced at the independent particle model level (Phillips and Kleinman 1959).²² But even at this level of approximation the Pauli principle between the core and valence electrons must still be satisfied, and (in contrast to the Hartree product) the Slater determinant is not separable into a simple product of core and valence Slater determinants. The generalized Phillips–Kleinman equation still couples valence and core orbitals and the term “*core–valence separation*” has to be understood in this context. Similar arguments apply for Kohn–Sham density functional theory²³ where the density cannot be separated into a valence and a core part. We refer to several important articles concerning these fundamental issues.²⁴

The different approximations to V_{CV} and V_{CC} will be discussed in the following. The general form of all effective core potentials (ECP), i.e., pseudopotentials (PP) as well as (*ab initio*) model potentials (MP) is

$$V_{CV}(r_{ai}) \approx -\frac{Q_a}{r_{ia}} + V_{CV}^a(r_{ai})$$

and (2)

$$V_{CC}(r_{ab}) \approx -\frac{Q_a Q_b}{r_{ab}} + V_{CC}^{ab}(r_{ab}).$$

Q_a is the charge of core a ($Q_a = Z_a - n_c^a$), where n_c^a is the number of core electrons at atom a , i.e., if there is no ECP on center a we have $Q_a = Z_a$, Z_a being the nuclear charge of atom a . For a small-core ECP of gold with 19 valence electrons describing the $5s$, $5p$, $5d$, and $6s$ electrons we obtain $Q_{Au} = 19$. There are a number of different approximations and techniques for obtaining ECPs for V_{CV} and V_{CC} .

Concerning first the second term in Eq. (2) we can assume that $V_{CC}^{ab}(r_{ab}) = \text{const.}$ for $r > r_{\min}$, r_{\min} being roughly the distance where the two cores start to overlap. In other words, ECPs should *not* be applied in regions $r < r_{\min}$ unless core–core overlap and core–polarization corrections are applied. Almost all ECPs published so far do not include such

corrections and there are only a few articles concerned with core–core repulsion corrections, used especially for large core ECPs.^{25–27} The size of this term at smaller bond distances is one reason for the preference of small-core ECPs. For example, a one-valence electron pseudopotential for Au ([Pt]-core) leads to bond distances for AuH and Au₂ which are 0.34 Å and 0.83 Å (!) too short because of the neglect of core-overlap effects.²⁸

The first term in Eq. (2) includes the well known ECP (V_{PP} or V_{MP}) and corrections to core–valence correlation and core–polarization effects (V_{Pol}). The latter effects are either neglected in the ECP approximation or taken into account by a core polarization potential,^{25,29}

$$V_{Pol}^a(r_{ai}) \approx -\frac{1}{2}\alpha_a^D \mathbf{f}_a^2 \quad (3)$$

leading to corrections in the one- and two-electron integral part which substantially increases the computer time. α_D is the dipole polarizability of core a and \mathbf{f}_a is the field at core a produced by all other surrounding charges (electrons and cores). Higher order pole corrections can be added as well.³⁰ The r^{-4} dependence of the \mathbf{f}_a^2 term

$$\mathbf{f}_a = \frac{\mathbf{r}_{ai}}{r_{ai}^3} g(r_{ai}) + \sum_{b \neq a}^{N_C} Q_b \frac{\mathbf{R}_{ab}}{R_{ab}^3} \quad (4)$$

needs the introduction of a cut-off function g leading to quite complicated one-electron integrals,³¹ as implemented, for example, in the program package MOLPRO.³² If a sufficiently small core is chosen core–polarization and core–valence correlation effects can safely be neglected. For example, a one-valence electron pseudopotential for Au leads to dissociation energies for AuH which is 0.6 eV too small because of the neglect of core–polarization and core–valence correlation effects. It is now clear that the effects of V_{CC} and V_{Pol} to molecular properties can only be neglected if a small core definition for the ECP is chosen. For Au a one-valence electron pseudopotential is clearly not a good choice and it will be seen in the next section if the choice of 11 valence electrons for Au ($5d^{10}6s^1$) is sufficient for the treatment of AuH.

For the choice of $V_{CV}^a(r_{ai})$ for atom a we distinguish between (*ab initio*) model potentials (MP) of Hyzina and co-workers,³³ which retain the inner nodal structure of the valence orbital, and pseudopotentials using nodeless valence orbitals (also called pseudo-orbitals).³⁴ Both ECP approximations are closely connected to the more general Phillips–Kleinman potential.^{22,35} In this paper we are only concerned with PPs. For a general introduction to the less widely used MP method, which is for example implemented in the MOLCAS4 program package,³⁶ and its relativistic extension, see Ref. 37. A comparison between PPs and MPs are given in Ref. 38. However, we mention that relativistic perturbation operators can in principle be directly used in the MP procedure since the orbitals retain their inner nodal structure.

We may choose the following local form for a PP at atom a ,

$$V_{PP}^a(r_{ai}) \approx \sum_{n=1}^{N_{fit}} c_n g_n(r_{ai}), \quad (5)$$

where the interaction with the core is modeled by a linear combination of N_{fit} fit functions. The pseudopotential V_{PP}^a (5) can be extended from a local to a semilocal or even nonlocal form as we shall see. There are various fitting techniques for Eq. (5) and its extensions. The fit functions g_n are usually chosen as Gaussian functions for the purpose of straight forward integral evaluation.³⁹ It is clear the semi- or nonlocal approximations allow for more flexibility in the adjustment procedure compared to local PPs. There is, however, another reason for not choosing local PPs. Consider a system with only one valence electron. The radial valence Hamiltonian is

$$H_V^{(l)} = -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{Q}{r} + V_{PP}(r) + \frac{l(l+1)}{2r^2}, \quad (6)$$

where $V_{PP}(r)$ is a local PP. Considering two different angular symmetries l and $l' = l+1$ we can write

$$H_V^{(l+1)} - H_V^{(l)} = \frac{l+1}{r^2}. \quad (7)$$

Since the operator on the right-hand side of Eq. (7) is positive we obtain the inequality for the eigenvalues,

$$\begin{aligned} \epsilon_i^{(l+1)} &= \langle f_i^{(l+1)} | H_V^{(l+1)} | f_i^{(l+1)} \rangle \\ &\geq \langle f_i^{(l+1)} | H_V^{(l)} | f_i^{(l+1)} \rangle \\ &\geq \langle f_i^{(l)} | H_V^{(l)} | f_i^{(l)} \rangle = \epsilon_i^{(l)} \end{aligned} \quad (8)$$

with the eigenfunctions $f_i^{(l)}$ to $H_V^{(l)}$. The first inequality follows directly from Eq. (7) whilst the second inequality follows from the variational principle. Equation (8) implies that within a fixed principal quantum number for a pseudovalence system a local approximation cannot alter the sequence in the angular momentum symmetries, i.e., we always obtain $\epsilon_s \leq \epsilon_p \leq \epsilon_d \leq \dots$ for the lowest eigenstates of each symmetry. To illustrate this we consider the $\text{Ca}^+ 4s \rightarrow 3d$ first valence excitation energy (13 650 cm^{-1}) which is *below* the $4s \rightarrow 4p$ (25 192 cm^{-1}) second valence excitation energy.⁴⁰ This situation cannot correctly be described by a two valence electron local PP. The proof outlined here only holds for one-valence electron systems but similar difficulties are obtained for the multielectron case.⁴¹ One should therefore choose l -dependent (semilocal) PPs.

Semilocal PPs are most widely used and chosen in the following form for atom a ,

$$V_{PP}^a(r_{ai}) \approx \sum_{n=1}^{N_L} A_n^a r_{ai}^{m_n^a} e^{-\alpha_n^a r_{ai}^2} + \sum_{l=0}^{L_{max}} \sum_{n=1}^{N_{SL}} B_{ln}^a r_{ai}^{m_{ln}^a} e^{-\beta_{ln}^a r_{ai}^2} P_{a,l} \quad (9)$$

with the operator

$$P_{a,l} = \sum_{m_l=-l}^{+l} |alm_l\rangle \langle alm_l| \quad (10)$$

projecting onto the Hilbert subspace of angular momentum l with respect to atom a ; and in Eq. (9) m is an integer with $m \geq -2$. It is a matter of choice if a local part [first term in Eq. (9)] is included in the PP or not. The summation in the semilocal part [second term in Eq. (9)] is often carried out to $L_{max} = \max\{l_{core}\}$, the maximum angular momentum found in the core orbital space.⁴² For the accuracy of the PP, however,

it is often necessary to sum up to $L_{\max} > \max\{l_{\text{core}}\}$. This is especially the case if large-core PPs are used or if the local part in Eq. (9) is neglected.

The following fit procedures are currently in use which distinguishes the different types of PPs:

(a) *Energy consistent pseudopotentials* (ECP). Here the PP parameters in Eq. (9) are adjusted to the spectrum of a specific atom a . This technique is used extensively by the Stuttgart group⁴³ where a least-squares fit to numerically obtained ionization potentials, electron affinities, and excitation energies ΔE_i^{AE} for the neutral and various charged ions of atom a is carried out,

$$\sum_i (\Delta E_i^{\text{AE}} - \Delta E_i^{\text{PP}})^2 = \min. \quad (11)$$

In most cases only up to two Gaussians ($N_{SL} = 2$) per angular symmetry l are required for this fitting technique. Reference energies are either taken from nonrelativistic all-electron (AE) numerical HF calculations yielding nonrelativistic pseudopotentials (NRPP) or from all-electron numerical relativistic procedures yielding scalar (or averaged) relativistic pseudopotentials (ARPP) if spin-orbit splitting is neglected. Deviations from the reference spectrum are usually in the order of 0.1 eV or less for the important valence space if small-core PP are used.

(b) *Shape consistent pseudopotentials* (SCPP). In this case the parameters in Eq. (9) are adjusted in such a way that the valence orbitals of each symmetry are reproduced above a certain cut-off radius R_c . There are different techniques to achieve this. Hay, Wadt, and Christiansen *et al.* modify the all-electron wave function in the core region to become nodeless. The pseudopotential HF equations are then used to reproduce these nodeless pseudoorbitals by adjusting the parameters in Eq. (9). This requires inversion of the Fock equation. The disadvantage of this procedure is that the inversion of the Fock equation produces l -dependent pseudopotentials which require a larger number of Gaussian in the fit procedure. This is avoided in a technique first applied by the Toulouse group⁴⁴ and later used by Stevens, Basch, Krauss, and co-workers. Here the 2-norm $\|O\|_2$ of the following operator is minimized:

$$O = \tilde{\epsilon}_\nu |\tilde{\varphi}_\nu\rangle \langle \tilde{\varphi}_\nu| - \epsilon_\nu |\varphi_\nu\rangle \langle \varphi_\nu|. \quad (12)$$

The so-called norm-conserving pseudopotential (NCPP) is a variant of the shape consistent PP developed by Bachelet, Schlüter, and co-workers.⁴⁵

Our previous work showed that energy adjusted PPs lead to accurate ionization potentials and excitation energies and reproduce the pseudo-orbitals extremely well in regions $R > R_c$, whilst shape consistent pseudopotentials can deviate from all-electron energies by 0.2 eV or more.^{1,2} Therefore, Maron and Teichteil very recently explored a multireference fitting procedure for SCPPs which significantly improves the spectrum of an atom.¹³

A different version of a semilocal PP derived from the normconserving fitting technique has been introduced by Titov, which he terms generalized pseudopotentials.⁴⁶ In this case the orbital space is divided into a core part, an outer core part and a valence part. Very recently Titov *et al.* dem-

onstrated that he can reproduce the valence spectrum of the Hg atom by one order of magnitude more accurate compared to the common semilocal PPs.⁴⁷ If this provides a considerable improvement compared to small-core energy consistent or multi-configurational shape consistent PPs for molecules has to be seen.⁴⁸

Nonlocal PPs are only used in the context of improved integral evaluation, i.e., semilocal PPs can be transformed to a linear combination of Gaussian type nonlocal operators which reduces matrix elements to a simple linear combination of overlap integrals (as in the case for MPs).⁴⁹

We finally address the problem of electron correlation in pseudopotential theory. Consider a two-electron, two orbital system with double substitution only. We obtain for the electron correlation energy,

$$E_{\text{cor}} = a + \Delta\epsilon - ((a + \Delta\epsilon)^2 + K_{HL}^2)^{1/2}, \quad (13)$$

with $\Delta\epsilon = \epsilon_L - \epsilon_H$, $a = (J_{HH} + J_{LL})/2 - 2J_{HL} + K_{HL}$. H and L denotes the HOMO and LUMO, respectively. Taylor expansion in Eq. (13) leads to the following dominant term:

$$E_{\text{cor}} = -K_{HL}^2 (2(a + \Delta\epsilon))^{-1}. \quad (14)$$

If we adjust the pseudopotential in such a way that $\Delta\epsilon(\text{PP}) = \Delta\epsilon(\text{AE})$ we see that the difference between the all-electron and pseudopotential electron correlation is critically dependent on the HOMO-LUMO exchange K_{HL} . Indeed, both Teichteil *et al.*⁵⁰ and Pittel and Schwarz⁵¹ found that $K_{HL}(\text{PP}) > K_{HL}(\text{AE})$ by up to 10% due to the nodeless structure of the pseudo-orbitals. This leads to an overestimation of the electron correlation contribution. A recent study by Dolg supports this argument.⁵² We note that accurately adjusted small core pseudopotentials may reduce this deficiency significantly and the simple model [Eq. (14)] may not be applied for many-electron systems or for differences in energies.

III. COMPUTATIONAL DETAILS

The Hartree-Fock (HF), Møller-Plesset second-order (MP2), coupled cluster singles-doubles (CCSD) and CCSD including triples perturbatively (CCSD(T)) methods using seven different scalar relativistic pseudopotentials were employed to calculate the spectroscopic properties of Au, Au⁺, and AuH. The pseudopotentials commonly used in *ab initio* and density functional calculations are listed in Table I. In addition we carried out nonrelativistic HF, scalar relativistic Douglas-Kroll (DK) HF (Ref. 53) and four-component Dirac-Hartree-Fock (DHF) all electron calculations as well as correlated calculations with these wave functions as references. For the all-electron calculations the uncontracted $25s23p14d10f$ basis set of Laerdahl *et al.*⁵⁴ was used for gold with the modifications notes in Ref. 18. For the PP calculations a subset of the all-electron basis set was employed for gold. It was generated by removing the highest exponent functions of the all-electron basis set to give an uncontracted $11s10p7d5f$ basis set. The high exponent functions left out in the PP calculations change the total energy by less than 10^{-3} a.u. and do not alter noticeably our calculated atomic and molecular properties. For hydrogen a Dunning augmented triple-zeta basis set without the diffuse f

TABLE I. Pseudopotential references and description.^a

Abbreviation	Description of the pseudopotential	Ref.
Sta19	ECPP Schwerdtfeger <i>et al.</i> (DHF)	16
Stb19	ECPP Andrae <i>et al.</i> (WB)	63
SK19	SCPP Stevens <i>et al.</i> (DHF)	64
CE19	SCPP Christiansen <i>et al.</i> (DHF)	65
HW19	SCPP Hay and Wadt (CG)	6
CE11	SCPP Christiansen <i>et al.</i> (DHF)	65
HW11	SCPP Hay and Wadt (CG)	6
NRSt19	ECPP Schwerdtfeger <i>et al.</i> (NR)	16

^aThe number in the first column denotes the number of valence electrons for the particular core definition. EC denotes energy consistent and SC shape consistent pseudopotential. The different relativistic approximations used in the fit procedure were spin-orbit averaged Dirac-Hartree-Fock (DHF), Wood-Boring (WB) (Ref. 66) and Cowan-Griffin (CG) (Ref. 67). NR denotes the nonrelativistic approximation.

function was used; uncontracted for all calculations. The GAUSSIAN98 (Ref. 55) and MOLCAS4 (Ref. 36) packages were used for all one-component calculations while the DIRAC (Ref. 56) program suite was used for all four-component calculations. The same active space was kept for all the correlated calculations and included all 20 valence electrons and all virtual orbitals up to 100 a.u. unless stated otherwise. We note that in the relativistic all-electron calculations the 4*f* shell lies energetically above the 5*s* shell and (if not mentioned otherwise) was not included in the active space. The counterpoise correction⁵⁷ was applied in order to correct the results for the basis set superposition error (BSSE) at various levels of approximation.

At the PP and DK level a 13 point potential energy curve was produced around the pre-optimized equilibrium geom-

etry of AuH. A rotational-vibrational analysis was then carried out using the Numerov-Cooley procedure as implemented in MOLCAS4.³⁶ The expense of the DHF calculations (approximately an order of magnitude higher than the DK calculations) precluded the calculation of a more accurate potential energy surface. Instead the force constant (k_e), dissociation energy (D_e), and equilibrium geometry (r_e) were calculated by a quadratic fit to three points at exactly $r=r_e$ and $r=r_3 \pm 0.01 \text{ \AA}$.

Polarizabilities were calculated for Au and Au⁺ using the finite field method with point charges of ± 5 , ± 10 , and ± 20 a.u. placed at ± 100 a.u. from the atomic center. This technique allows the efficient calculation of CCSD(T) polarizabilities.

IV. RESULTS AND DISCUSSION

The calculated atomic properties for a variety of PPs in comparison with all-electron results are given in Table II. We note that our all-electron DK and DHF CCSD(T) ionization potentials (IP) and electron affinities (EA) are in excellent agreement with the more precise Fock-space CCSD DHF plus Breit correction results of Eliav *et al.*⁵⁸ At the HF level all PPs yield results in excellent agreement with the all-electron IPs and EAs for Au even for the large core PPs. For the energy adjusted PPs this is of course expected.¹ At the correlated level we obtain a similar picture perhaps with the exception of the HW 11 PP. Compared to the all-electron DK or fully relativistic DHF results we cannot detect significant overestimation of electron correlation effects by the pseudopotential method for either the IP or EA of gold.

TABLE II. Polarizabilities (α_D), electron affinities (EA), and ionization potentials (IP) for gold and the gold cation.^a

	HF				CCSD				CCSD(T)			
	IP	EA	α_D (Au ⁺)	α_D (Au)	IP	EA	α_D (Au ⁺)	α_D (Au)	IP	EA	α_D (Au ⁺)	α_D (Au)
Exp									9.23	2.31		
DHF-limit	7.67	0.67										
AE/DHF	7.69	0.67	11.8	47.3	9.05 ^c	2.08 ^c	12.7 ^c	36.8 ^c				
AE/DK	7.63	0.64	11.7	47.8	8.96 ^d	2.03 ^d	12.5 ^d	37.1 ^d	9.09 ^d	2.21 ^d	12.8 ^d	36.1 ^d
					9.02 ^c	2.06 ^c	12.6 ^c	35.8 ^c	9.13 ^c	2.23 ^c	12.9 ^c	34.8 ^c
					8.90 ^b	1.99 ^b	12.3 ^b	37.6 ^b	8.99 ^b	2.14 ^b	12.6 ^b	36.8 ^b
Sta19	7.69	0.62	11.6	49.0	9.03	2.05	12.5	36.4	9.13	2.22	12.7	35.5
Stb19	7.69	0.62	11.8	49.3	9.03	2.06	12.8	36.5	9.14	2.23	12.8	35.6
CE19	7.71	0.63	11.8	49.1	9.07	2.08	12.6	36.4	9.18	2.26	12.9	35.4
SK19	7.65	0.61	11.9	50.3	8.99	2.05	12.8	37.2	9.11	2.23	13.0	36.1
HW19	7.82	0.68	11.9	47.3	9.19	2.15	12.8	35.5	9.31	2.34	13.1	34.6
CE11	7.74	0.65	11.8	51.1	8.95	2.04	12.0	36.2	9.02	2.16	12.2	35.5
HW11	7.60	0.59	11.5	53.0	8.77	1.94	11.8	37.4	8.83	2.05	12.0	36.7
AE/NR	5.93	0.08	10.2	108.4	6.92 ^d	1.04 ^d	10.9 ^d	68.2 ^d	7.01 ^d	1.15 ^d	11.0 ^d	63.8 ^d
					6.93 ^c	1.04 ^e	10.9 ^e	68.0 ^e	7.02 ^c	1.16 ^e	11.1 ^e	63.8 ^e
					6.95 ^c	1.05 ^c	10.9 ^c	67.3 ^c	7.04 ^c	1.16 ^c	11.1 ^c	63.2 ^c
					6.86 ^b	1.01 ^b	10.6 ^b	70.4 ^b	7.08 ^b	1.11 ^b	10.8 ^b	66.4 ^b
NRSt19	5.94	0.08	10.2	108.0	6.95	1.05	11.0	67.7	7.04	1.16	11.1	63.3
HF-limit	5.92	0.10										

^a α_D in a.u., IP and EA in eV. HF and DHF limits results from Ref. 28. For all pseudopotential calculations the active occupied orbital space is (5*s*5*p*5*d*5*s*) for the CCSD and CCSD(T) procedure.

Active occupied orbital spaces in the all-electron procedures:

^b(5*d*6*s*);

^c(5*p*5*d*6*s*);

^d(4*f*5*s*5*p*5*d*6*s*);

^e(5*s*5*p*5*d*6*s*).

TABLE III. Spectroscopic constants for AuH at the HF level using various all-electron and pseudopotential methods.^a

	DHF	DK	Sta19	Stb19	SK19	CE19	HW19	CE11	HW11	NRS19	AENR
r_e	1.570	1.576	1.574	1.575	1.579	1.570	1.561	1.592	1.626	1.829	1.830
D_e	1.793	1.736	1.695	1.702	1.691	1.720	1.772	1.660	1.425	1.077	1.096
ω_e	2095	2062	2068	2071	2064	2088	2130	2024	1897	1481	1475
$\omega_e x_e$		-32.3	-36.8	-37.1	-36.8	-37.1	-38.0	-33.6	-30.2	-24.7	-22.2
B_e		6.772	6.776	6.768	6.739	6.815	6.892	6.625	6.352	5.022	5.018
α_e		0.196	0.186	0.185	0.185	0.187	0.191	0.164	0.147	0.122	0.127
C_e		2.89	2.96	2.94	2.92	2.95	2.92	2.90	2.92	2.14	2.31
μ_e	2.55	2.62	2.57	2.58	2.62	2.56	2.42	2.68	2.82	4.89	4.91

^aThe Dunham notation is used. Equilibrium bond distances r_e in Å, dissociation energies D_e in eV (not corrected for zero-point vibrational contributions), vibrational frequencies ω_e , anharmonicity constants $\omega_e x_e$, rotational constants B_e , and rotational-vibrational coupling constant α_e in cm^{-1} , and centrifugal distortion constant C_e in 10^{-4} cm^{-1} , dipole moments μ_e in Debye.

The static dipole polarizability of atoms and ions is a property that is sensitive to the accuracy of the wave function in the valence region^{59,60} and is therefore ideal to demonstrate the accuracy of the pseudopotential approximation at the atomic level. As shown in Table II the variation in all the sets of data are relatively small for all small-core PPs and the data are in good agreement with the more extensive all-electron calculations. Perhaps the only exception is the HW19 PP, where the polarizability for neutral gold is underestimated by $\approx 2\%$ at the CCSD(T) level while the HW11 PP overestimates the polarizability by approximately the same amount. A comparison with the other pseudopotentials points to deficiencies in the fitting procedure. The relativistic results for the other pseudopotentials show no significant deviations from the AE data and are of similar quality compared to the nonrelativistic results, thus supporting the idea that relativistic effects can safely be incorporated into the pseudopotential approximation without any major difficulties.

We mention that the change in the polarizability due to electron correlation, relativistic effects or change in the type of pseudopotential applied is inversely proportional to the change in the ionization potential. This relationship between the polarizability and the ionization potential has previously been pointed out.^{59,61} Hence, if the ionization potential is too low the polarizability is too high as in the case of HW11 PP. This may lead to an overestimation of dispersion interactions in weakly interacting systems. Hence, it is important that ionization potentials (and excitation energies) are correctly obtained in the pseudopotential fit procedure as this is case for the ECPPs.

At both the all-electron relativistic DK and nonrelativistic level of theory we explored electron correlation contributions coming from different subspaces of the $(4f5s5p5d)$ core of gold. The results are shown in Table II. The data clearly show that an accurate polarizability for neutral Au is only obtained if correlation from the $(5s5p)$ core is included, especially at the relativistic level. For example, both the ionization potential and the electron affinity of Au are underestimated if the $(5s5p)$ electrons are not explicitly correlated which reflects the situation in the 11 valence electron PPs. Thus the use of large core PPs for gold will not be a good choice unless core-polarization and core-valence correlation is included in the form of for example Eq. (3). The latter choice, however, may still not be sufficient because the $(5s5p)$ orbitals considerably overlap with the $(5d6s)$ orbitals.

The question remains if pseudopotentials can successfully be transferred from the atomic to the molecular level. The spectroscopic constants for AuH calculated for the individual pseudopotentials and all-electron methods at the HF and MP2 levels are compared in Tables III and IV. The maximum and minimum deviations are shown in Table V. The coupled cluster calculations for both the NR and R Stuttgart PPs are shown in Table VI and compared with experimental data.

The maximum absolute deviation of the 19 valence electron PPs from the DK results is at the SCF/MP2 level 0.015/0.014, 0.045/0.273, 68/70, and 0.20/0.20 for r_e , D_e , ω_e , and μ_e , respectively. The same data for the DK compared to the DHF result is 0.006/0.002, 0.06/0.17, 33/4, and 0.07/0.04. For the maximum absolute deviation of uncorrected

TABLE IV. Spectroscopic constants for AuH at the MP2 level using various all-electron and pseudopotential methods.^a

	DHF	DK	Sta19	Stb19	SK19	CE19	HW19	CE11	HW11	NRS19	AENR
r_e	1.484	1.486	1.479	1.480	1.484	1.477	1.472	1.519	1.547	1.689	1.694
D_e	3.208	3.034	3.137	3.161	3.144	3.193	3.307	2.520	2.450	1.955	1.955
ω_e	2521	2517	2522	2523	2518	2542	2587	2303	2156	1726	1716
$\omega_e x_e$		48.4	44.7	44.6	44.5	44.5	44.7	40.7	37.1	30.0	27.1
B_e		7.624	7.678	7.669	7.634	7.707	7.757	7.280	7.016	5.885	5.861
α_e		0.213	0.214	0.213	0.212	0.214	0.212	0.194	0.183	0.144	0.157
C_e		2.81	2.85	2.83	2.81	2.83	2.78	2.94	3.02	2.82	2.69
μ_e	1.03	1.07	1.01	1.01	1.04	0.99	0.87	1.08	1.20	3.40	3.43

^aThe Dunham notation is used (see Table III for details).

TABLE V. Maximum and minimum deviations in spectroscopic constants from the all-electron DK result for AuH at the HF and MP2 level.^a

	HF				MP2			
	19VEPP	11VEPP	Sta19	NRSt19	19VEPP	11VEPP	Sta19	NRSt19
r_e	-0.015	+0.050	-0.002	-0.001	-0.014	+0.061	-0.007	-0.005
	-0.001	+0.016			-0.002	+0.033		
D_e	-0.045	-0.311	-0.041	-0.019	+0.273	-0.584	+0.103	0.000
	-0.016	-0.076			+0.103	-0.514		
ω_e	+68	-165	+4	+6	+70	-361	+5	+10
	+2	-38			+1	-214		
μ_e	-0.20	+0.20	-0.05	-0.02	-0.20	+0.13	-0.06	-0.03
	0.00	+0.13			-0.03	+0.01		

^aThe Dunham notation is used (see Table III for details). 19 VEPP: chosen from the set of all 19 valence electron PPs; 11 VEPP: chosen from CE11 and HW11. The Sta19 and NRSt19 deviations from all-electron results are listed as well.

compared to the corrected BSSE CCSD(T) level results we have 0.017, 0.101, 70 for r_e , D_e , and ω_e . From this we get the following important information:

(i) Scalar relativistic PPs show the same behavior as NR PPs (compare between the deviations of Sta19 and NRSt19). The minute larger deviations between the two relativistic procedures (DK and ARPP) compared to the nonrelativistic values for some properties can easily originate from the different definition of the scalar relativistic operator used, i.e., J -averaging energies, densities, orbitals or using truncated scalar relativistic operators will lead to different results.

(ii) The deviations at the correlated level are not significantly larger compared to the deviations at the HF level except perhaps for the AuH dissociation energy. 19 valence electron PPs overestimate correlation effects for the dissociation energy but this effect is relatively small (≈ 0.1 eV for Sta19) compared to basis set incompleteness, basis set superposition errors (see below) or insufficient treatment of electron correlation.

(iii) The 11 valence electron PPs give inferior results and show large errors in many properties, especially the dissociation energy which is severely underestimated due to the neglect of core–valence correlation and core–polarization effects. As mentioned before, the ($5s5p$) and ($5d6s$) charge distributions are not well separated. Furthermore, a pseudo-

orbital transformation for the $6s$ orbital leads to large changes in the inner part of the density where one still expects large overlap with the $5d$ orbital leading to errors in the $6s$ – $5d$ interaction at both the SCF and correlated level.

BSSE effects change the bond lengths to values closer to the experimentally determined result. The results clearly show that when large basis sets and high-level correlation techniques, such as CCSD(T), are combined it is possible to achieve near-experimental accuracy using the pseudopotential approximation. Further accuracy will be achieved if g or higher momentum functions are included in the basis set.⁶²

The comparison of DHF, DK, and PP methods proves that for AuH spin–orbit effects are minor, as there is no significant difference between the 4-component and scalar relativistic DK calculations except for the dissociation energy at the MP2 level. Lee *et al.* showed that spin–orbit coupling is estimated to contribute <0.001 Å to r_e , <7 cm⁻¹ to ω_e , and <0.03 eV to D_e for AuH.¹⁹ Spin–orbit coupling effects in pseudopotential theory is the subject of a subsequent paper in this series.

V. CONCLUSIONS

The variation between the scalar relativistic all electron and pseudopotential calculations is too small to be regarded as significant. Our results demonstrate that pseudopotentials are capable of yielding results which are not significantly different to all-electron calculations. It is also apparent that the correct choice of the core size is important. The large core (11 VE) pseudopotentials show sizeable differences when compared with the AE and 19 VE PP results. We therefore conclude that the relativistic pseudopotential method is an accurate, reliable and very efficient alternative to more computer intensive all-electron relativistic methods.

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TABLE VI. Spectroscopic constants for AuH at the CCSD(T) level using the Stuttgart pseudopotential.^a

expt.	Sta19		NRSt19		
		+BSSE		+BSSE	
r_e	1.524	1.510	1.527	1.730	1.747
D_e	3.08	3.230	3.124	2.157	2.086
ω_e	2305	2328	2306	1594	1575
$\omega_e x_e$	43.1	44.9	45.6	34.6	30.3
B_e	7.240	7.342	7.237	5.576	5.532
α_e	0.214	0.214	0.208	0.165	0.146
C_e	2.790	2.915	2.826	2.843	2.693
μ_e	...	1.017	...	3.368	...

^aThe Dunham notation is used (see Table III for details). Experimental data was taken from Huber and Herzberg (Ref. 17). The dissociation energy (D_e) is not corrected for zero-point vibrational energy contributions (ZPVE), i.e., the ZPVE was subtracted from the experimental dissociation energy of $D_0=3.22$ eV. +BSSE denotes that the basis set superposition error has been incorporated using the counterpoise method (Ref. 57).

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