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Electronic structure of Rh, RhH, and Rh$_2$ as derived from *ab initio* configuration interaction calculations

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The electronic structure of Rh, RhH, and Rh$_2$ in their ground and low-lying electronic states has been studied using nonempirical relativistic pseudopotentials and moderately large basis sets including f-type functions. The energy splitting ^4F–^2D, ionization potential and electron affinity of Rh have been obtained and compared with experimental results. A rather good agreement being found in all cases. For RhH the $^3\Delta$, $^3\Pi$, $^3\Phi$, $^3\Sigma^-$ and $^1\Sigma^+$ electronic states were studied. The ground state being $^3\Delta$ in agreement with previous theoretical studies. The calculated D_e for RhH was found to be in a nice agreement with the experimental value. For Rh$_2$ eight electronic states symmetrically dissociating into the ground state of the isolated atoms have been selected. Moreover a search for lowest electronic states has also been performed among those electronic states dominated by electronic configurations which (at r_e) do not correlate with the ground state of the isolated atoms. The lowest electronic state was a $^5\Delta_u$, the D_e corresponding to this state is 1.500 eV which is only 62% of the experimental value. The possibility of a metal–metal multiple bond in Rh$_2$ has also been considered by studying the lowest $^1\Sigma^+$ electronic state. This state was found to lie higher than all the quintuplets considered in this work.

INTRODUCTION

The theoretical study of small molecules containing transition metal atoms is one of the most active areas in quantum chemistry because the challenge it represents in many cases. Thus, while a very extensive study has been done on first and second row transition metal hydrides,[1,2] and oxides,[3–6] the information about transition metal dimers is more scarce,[6–8] especially for second-row transition metal dimers where accurate studies have been carried out mainly for Ag$_2$[9] and very recently for Pd$_2$.[10] A set of CASSCF calculations for Y$_2$, Nb$_2$ and Mo$_2$ was also reported by Walch and Bauschlicher.[11] Additional information about transition metal dimers can be found on the series of reviews appeared in the past few years.[6–8]

Despite the great importance of rhodium as a constituent of many catalysts,[12,13] the electronic structure of Rh$_2$ remains unknown. In fact, Rh$_2$ is surely the least studied transition metal dimers. The only *ab initio* calculations being that reported by Shim[14] at the all electron plus valence CI (configuration interaction) level. A very recent CASSCF/MRCI study of the 30 lowest roots of the CASSCF has also been reported by Balasubramanian and Liao.[15] However, the basis set used in this study was rather limited and the selection of the electronic states was carried out by studying the lowest roots of a state averaged CASSCF calculation. As it will be shown, there are some low-lying electronic states, dissociating into the ground state of the

isolated atoms, which do not appear by using that procedure. Moreover, the ground state found in the present work is also different from the one reported in Ref. 15.

Because its important role on the so-called strong metal support interactions (SMSI)[16,17] our group is interested in the chemisorption of atomic hydrogen on small rhodium clusters. However, due to the lack of theoretical information about Rh$_2$, and the very limited one for RhH[2,18] a systematic study of the electronic structure of Rh, RhH, and Rh$_2$ seems to be mandatory. This is indeed the aim of the present work.

COMPUTATIONAL DETAILS

Present calculations were carried out using a relativistic nonempirical pseudopotential[19–21] leaving explicitly the $4d^8 5s^1$ valence electrons of rhodium. This relativistic pseudopotential includes mass-average velocity and Darwin corrections and has been obtained to describe the two low-lying states of Rh simultaneously.

In order to test the accuracy of the present methodology three different basis sets were used for Rh. The first one is a $3s,2p,4d$ contraction of the $5s,3p,6d$ primitive set which was optimized at the SCF level. Contraction scheme were $3 + 1 + 1$ for the s-shell, $2 + 1$ for the p-shell and $3 + 1 + 1 + 1$ for the d-one. This basis set may be denoted as (536/324) and will hereafter referred as Basis 1. The second one includes a set of three primitive f functions contracted to one, the exponents and coefficients being taken from Ref. 2 and Ref. 22 respectively. This basis is denoted as (5363/3241) and referred as Basis 2. Finally, one s and d

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diffuse primitive was optimized for Rh-, at the SCF level, and added to the previous basis set and the p set was left uncontracted. Moreover an even tempered f-function was added to the f set, the corresponding exponent being also taken from Ref. 2. This basis set is denoted as (7374/4352) and referred as Basis 3.

The atomic hydrogen basis set is derived from a $4 + 1 + 1 + 1$ and $2 + 1 + 1$ contraction of the $7s,4p,1d$ primitives. This basis set is derived from the Van Duijneveldt basis set[22] augmented by an even tempered diffuse s function. The p primitives correspond to four term expansion of a Slater orbital with an exponent of 1.0, and the d exponent was taken as 1.63. This basis set is then of (741/431) quality, it is formally identical to that used in Ref. 2 but includes an extra d function.

Atomic integrals were obtained by means of PSHONDO[24] program, a modification of the HONDO package[25] including the nonempirical pseudopotential code. One electron functions were obtained at the ROHF level using a monoconfigurational version of the elementary Jacobi rotations MCSCF program of Carbo et al.[26,27]

Electronic correlation was introduced by means of the three-class CIPSI algorithm.[28-30] Since the CIPSI method has been reviewed recently in a series of papers[31-33] let us only say that the method is based on the definition of a multireference space which contains the more important determinants. The determinants belonging to this class are taken as generators and constitute the G space. Each determinant belonging to G generates all its single and double excitations which constitute the GD class. Those determinants belonging to GD but having a noticeable contribution to the wave function constitute the M class. In practice, the G space is iteratively constructed so as to include all generated determinants whose contribution to the first-order wave function is larger than a certain first threshold (η). Those determinants having a contribution between η and a second threshold (τ) constitute the M class.

The correlation energy is calculated in two parts: A variational one obtained through diagonalization of the restriction of the Hamiltonian to the $G + M$ space, and a perturbational one which takes the effect of those determinants in GD not belonging to M up to second order. The method may be viewed as a multireference many-body perturbation one in which G defines the zero-order wave function, the effect of determinants belonging to M being taken into account up to infinite order and that of the remaining determinants up to second order.

In the present work no extrapolation nor Davidson correction were used. As recently shown, those empirical corrections are very small for the hydrides[34] and may be too large for Rh₂ (*vide infra*).

Dissociation energies were obtained as in Ref. 34 and spectroscopic parameters were determined by adjusting the calculated energy curves to a three-degree polynomial. The use of a calculation for the atoms at infinite separation and in their ground state is unavoidable, specially is some of the studied states do not correlate with this proper limit. The computation of D_e by difference between the energy at r_e and at a distance of about 10 a.u. is inappropriate, in these

cases, and may lead to a too large value for the dissociation energy as in Ref. 15

It is worth pointing out that according to the CIPSI philosophy the reference space for each electronic space is individually constructed. This means that the MRCI is different for each electronic state and that it is iteratively constructed to include as references the more important determinants. In this way all the electronic states have wave functions of similar quality. Moreover, although widely used, we would like to point out that there is no special arguments favoring the CASSCF/MRCI approach against any other MRCI scheme except for the ability of the CASSCF/MRCI to handle with a larger variational problem due to its computational features. However, there is a price to be paid and it is the *a priori* selection of the reference space which, in some cases, may not be adequate enough. Depending on the active orbitals, it is possible to have generated determinants having a contribution to the wave function larger than that of some reference determinants.

ATOMIC CALCULATIONS

As it is well-known transition metal chemistry is strongly dominated by the energy separation between the two lowest asymptotes arising from atomic configurations with different "d" occupations.[1,2,5-8] In the case of atomic rhodium these are ^4F and ^2D arising from d^8s^1 and d^9 electronic configurations, respectively. The experimental splitting being of only 0.34 eV[35] as resulting from a weighted average over fine structure components.

Results in Table I show that the calculated energy separation is in a reasonable agreement with experimental data. The result is rather insensitive to the presence of f functions in the basis set. This is not surprising since it is known that second-row transition metal atoms are less basis set demanding that those of the first row ones, although extensive inclusion of electronic correlation is more important (See Ref. 6 and references therein). With respect to the previous results reported by Langhoff et al.,[2] the difference is rather large, the present value being less accurate than the one earlier reported in Ref. 2. This is due to the different pseudopotential used in Ref. 2 and in the present work. In fact, while only the nine ($4d^8 5s^1$) valence electrons are treated explicitly

TABLE I. Atomic energy separations (^4F-^2D), ionization potential and electroaffinity of Ih as obtained at the SCF and CI levels through the use of different basis sets. All data are in eV.

	Basis 1 (3s2p4d)		Basis 2 (3s2p4d 1f)		Basis 3 (4s3p5d 2f)	
	SCF	CI	SCF	CI	SCF	CI
^4F-^2D	2.31	0.73	2.31	0.83	2.31	0.71
Experimental value Ref. 33: 0.34						
Langhoff *et al.* Ref. 2: 1.41 (SCF) and 0.59, 0.47 (SDCI, CPF)						
IP	6.27	6.78	6.27	6.99	6.27	7.26
Experimental value Ref 33: 7.46						
EA	−0.45	0.59	−0.45	0.60	−0.21	0.59
Experimental value Ref. 35: 1.12 + 0.1						

here, the relativistic ECP used in Ref. 2 also included the $4s^2 4p^6$ electrons in the valence shell although only nine electrons were then correlated. The effect of explicitly considering the $4s^2 4p^6$ electrons is to considerably reduce the energy difference at the SCF level (See Table I). Although the atomic energy separation between ^4F and ^2D of Rh is not as accurate as the value reported by Langhoff *et al.* Ref. 2, the influence on the calculated molecular parameters should not be very large as deduced from the results reported in the next section.

Further information about the quality of present calculations can be found from the values reported for the ionization potential (IP) and electron affinity (EA) of Rh (Table I). These values were obtained by difference between the energy obtained either at the SCF or CI level of atomic Rh in its ^4F ($4d^8 5s^1$) ground state, and the one corresponding to the cation (^3F, $4d^8$) and anion (^3F, $4d^8 5s^2$), respectively. Again it is shown that the effect of including *f* functions in the atomic basis set is very small. Moreover, the final value for the EA is still far from the experimental value[36] and the effect of adding diffuse *s* and *d* functions is very small at the CI level. This is because the exponents for the diffuse primitives were optimized at the SCF level. The calculated value for the IP is in reasonable agreement with experiment. In the atomic calculations reported in the present section the dimension of the *G*, *M* and *GD* subspaces was of about 350, 3000, and 560 000 determinants, respectively. The perturbational contribution to the electronic correlation never exceeded 10% of the total value.

In the view of the results reported in the present section it was decided to perform the molecular calculations using only Basis 2. Although the effect of *f* functions is in fact small, it is necessary to include, at least partially, angular correlation of the *d* electrons and may have a non-negligible effect on the calculated molecular properties.

GROUND AND LOW-LYING STATES OF RhH

The metal–hydrogen bond is usually dominated by the $n_s - s_H$ interaction[1,2] and the lowest electronic states arise from the different occupation of the *d* orbitals which (in the $C_{\infty v}$ punctual group) are split into σ, π, and δ components. In this way, the lowest electronic states arising by interaction of atomic hydrogen with atomic Rh (in its ^4F electronic ground state) are $^3\Delta$, $^3\Pi$, $^3\Phi$, and $^3\Sigma^-$. Likewise, there is evidence[18] for rather low-lying states of $^1\Sigma^+$ symmetry arising from the ^2D asymptote.

Previous theoretical studies using a relativistic ECP dealing explicitly with 17 electrons and large basis sets (including also *f* functions) have already been reported for the three ($^3\Delta$, $^3\Pi$, $^3\Phi$) low-lying states, although $4s^2 4p^6$ electrons were not correlated. In addition $^3\Sigma^-$, $^1\Sigma^+$ (and four other electronic states) were considered in a recent work by Balasubramanian and Liao.[18] In this case only the $d^8 s^1$ electrons were explicitly treated, the basis set did not include *f*-type functions but spin–orbit relativistic corrections were accounted for.

In the present work the $^3\Delta$, $^3\Pi$, $^3\Phi$, $^3\Sigma^-$, $^1\Sigma^+$. Electronic states have been studied. This will permit a compari-

son of results with and without *f* functions, with and without explicitly including the $4s^2 4p^6$ electrons of Rh and will provide a further test on the reliability of results obtained for Rh$_2$.

Since in this case it is clear which states are to be treated, the CI calculations were always started from the one-electron functions (MOs) derived from a ROHF calculation and using Basis 2 for atomic Rh. The threshold values used in this case (within the CIPSI algorithm) to select the *G* and *M* subspaces were 0.015 and 0.0015, respectively, leading to dimensions between 70 and 130 determinants for *G*, 3000–5000 for *M* and about 10^6–2.10^6 for the subspace of generated determinants *GD*.

The spectroscopic parameters for the five electronic states studied in the present work are given in Table II were the previous data reported in Refs. 2 and 18 have been included for comparative purposes. Results reported in Ref. 2 were obtained using different methods to include correlation effects, namely SDCI, MCPF, and CPF. However, since all these results were quite similar only those obtained through CPF have been included in Table II and the reader is referred to the original paper for further information. The corresponding potential energy curves are reported on Fig. 1.

The ground state is predicted to be a $^3\Delta$, in agreement with the recent works of Langhoff *et al.*[2] and Balasubramanian and Liao.[18] The calculated dissociation energy is somewhat smaller than previous results, although in a very good (perhaps fortuitous) agreement with experiment. The value for D_e is 2.55 eV to be compared with an experimental one of about 2.56 eV reported quite recently by Tolbert and Beauchamp.[37]

TABLE II. Calculated spectroscopic constants for the five low-lying states of RhH. Data are in angstroms for equilibrium internuclear distance (r_e), cm^{-1} for vibrational frequency (ω_e) and eV for the dissociation energy with respect to the $^4F + {}^2S$ asymptote (D_e) and transition energies (T_e).

		r_e	ω_e	D_e	T_e
$^3\Delta$					
	PW[a]	1.521	2054	2.55	0
	CPF[b]	1.579	2063	2.83	0
	MRCI[c]	1.540	2027	2.81	0
	Exptl.	⋯	⋯	2.56	0
$^3\Pi$					
	PW	1.599	1827	1.99	0.56
	CPF	1.638	1811	2.25	0.56
	MRCI	1.620	1779	2.25	0.58
$^3\Phi$					
	PW	1.589	1843	2.14	0.41
	CPF	1.663	1708	2.02	0.79
	MRCI	1.610	1822	2.31	0.53
$^3\Sigma^-$					
	PW	1.536	2097	1.99	0.56
	MRCI	1.610	1822	2.25	0.58
$^1\Sigma^+$					
	PW	1.500	2364	2.21	0.34
	MRCI	1.560	2052	2.41	0.42

[a] PW: Data obtained in the present work through the three-class CIPSI algorithm.
[b] CPF: Coupled perturbed formalism results taken from Ref. 2
[c] MRCI: Multireference study and doubles CI starting from a CASSCF calculation. Data from Ref. 17.
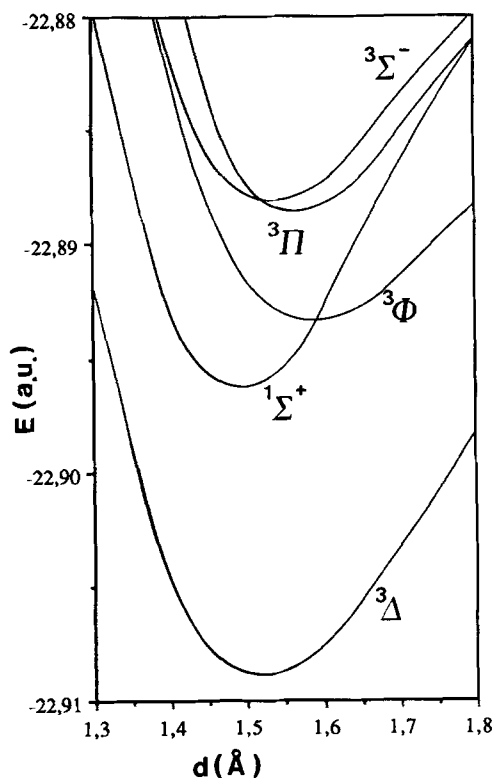
FIG. 1. Potential energy curves for the low-lying states of RhH considered in this work.

The values for r_e, ω_e, D_e and T_e reported in the present work are in a very good agreement with earlier calculations[2,18] although some remarks are necessary. With respect to the D_e and T_e values the three sets of calculations are in general quite comparable. However, present values for D_e are usually smaller by 0.2 eV than those reported in Refs. 2 and 18 although there is a nice agreement between the transition energy (T_e) values, specially with those obtained through CASSCF/MRCI reported in Ref. 18, indicating the need for a multireference treatment particularly for the excited states. The present values for the equilibrium distance are always shorter than the previous ones[2,18] although they are closer to the MRCI[18] values than those of the CPF[2] ones.

With respect to the accuracy of the present results it is worth pointing out that the second order perturbational contributions to the correlation energy derived from the *GD* determinants is never greater than 7% of the total value, even its dimension is very large (about 10^6).

The contribution of different electronic configurations to the total wave function is very similar to that reported in Ref. 18 and needs no further comment. The only point not raised in previous works is that RhH is already bounded at the SCF level although the D_e obtained at this level is only of 35% of the total value.

From the present results it seems clear that inclusion of *f*-type functions in the basis set is not necessary, nor it is

necessary to explicitly consider the $4s^2 4p^6$ electrons of Rh at least as far as RhH is concerned.

GROUND AND LOW-LYING STATES OF Rh₂

In the previous study of metal dimers by Shim,[14] carried out at the all electron level and using rather limited valence CI, a $^5\Sigma_g^+$ ground state was found for Rh_2, the leading configuration arising from a $\pi_u^3 \, \delta_g^3 \, \delta_u^3 \, \pi_g^3$ open-shell occupation. Moreover, a set of low-lying electronic states was also found. A more sophisticated study has been reported very recently by Balasubramanian and Liao.[15] In this study the lowest roots of an averaged valence CASSCF calculation were selected for each symmetry and followed by a MRCI calculation using the more important configurations of the CAS space as references. Among the 30 electronic states studied in Ref. 15 the lowest one was a $^5\Delta_g$ arising from an $1\sigma_g^2, 2\sigma_g^2,$ $\sigma_u^1, \delta_g^4, \delta_u^3, \pi_u^4, \pi_g^2$, electronic configuration. However, unless a change on the leading configuration occurs at larger distance this electronic state does not properly dissociate in the ^4F electronic state of the separated atoms. In fact, since as reported in Ref. 15, it dissociates to the $d^8 s^1$ limit of the separated atoms, the electronic configuration of the separated atoms must be $d_\sigma^2 \, d_\pi^3 \, d_\delta^3 \, s^1$ and $d_\sigma^1 \, d_\pi^3 \, d_\delta^4 \, s^1$. The former can lead to a ^4F but the latter cannot. This point is important because the way in which the dissociation energy is computed in Ref. 15, i.e., by difference between the energies computed at the equilibrium distance and at about 15 a.u. may not be correct enough, specially because one does not know where and how the configuration change takes place, and state averaged CASSCF one-electron functions are being used. Indeed, potential curves were not reported on Ref. 15.

Instead of selecting the electronic states as lower roots of a small CI or CASCI matrix the following approach was adopted: In a first step only those states directly correlating with the $^4Fg \times {}^4Fg$ asymptote were considered. Moreover, only those Fg arising from configurations with an even number of electrons in the σ, π, and δ subspaces were allowed to ensure a symmetrical dissociation. This excludes all the states of "ungerade" symmetry. Secondly, two extreme situations were considered. On the one hand the possibility of a single-bond with the *d*-shell electrons of each Rh coupled in a ferromagnetic way, leading to states of multiplicity equal to five. On the other hand the possibility of a multiple metal–metal bond formation, in this case the electronic ground state will be a $^1\Sigma_g^+$ dominated by the closed shell determinant and probably mixed with the antiferromagnetic electronic configuration, with the electrons coupled to give a singlet state. According to these considerations the states to be studied are of quintuplet and singlet multiplicity. In the singlet case, the spatial symmetry is also clear but several possibilities still exist for the quintuplets according to their open-shell occupation.

To decide among the several quintuplets dissociating into the ground state of the separate atoms a set of valence CASCI calculations was carried out starting from a set of one-electron functions obtained at the SCF level for the $^5\Sigma_g^+$ described by Shim as the ground state. Then, a series of preliminary CIPSI calculations were carried out to try to distin-

TABLE III. Calculated spectroscopic parameters for the low-lying states of Rh2. Data are as in Table II.

	r_e	ω_e	D_e	T_e
$^5\Delta_u$	2.673	238	1.500	0.0
$^5\Sigma_g^+$ (I)	2.577	255	1.410	0.092
$^5\Delta_g$ (I)	2.607	229	1.191	0.309
$^5\Delta_g$ (II)	2.825	138	1.040	0.460
$^5\Sigma_g^-$	2.824	178	0.970	0.530
$^5\Sigma_g^+$ (II)	2.453	327	0.750	0.750
$^5\Pi_g$	2.787	224	0.450	1.050
$^5\Sigma_g^+$ (III)	2.831	155	0.250	1.250
$^5\Phi_g$	2.686	168	−0.004	1.504
$^1\Sigma_g^+$	2.634	183	−0.060	1.560

guish between the almost near-degenerate electronic states obtained in this way. From this set of calculations the $^5\Sigma_g^+$ arising from a $\pi_g^2 \, \pi_u^2$ open-shell occupation seemed to be the lowest one. Accordingly, the valence CASCI calculations were carried out again but starting from the MOs corresponding to this electronic configuration. At this level the order of electronic states is only slightly changed when changing the one electron functions and the total energies were, in all cases, rather independent of the starting MOs.

It was then decided to study the low lying roots of the CASCI matrix. These were three states of $^5\Sigma_g^+$ symmetry, the lowest $^5\Sigma_g^-$, $^5\Pi_g$, $^5\Delta_g$, and $^5\Phi_g$, electronic state. Moreover, $^1\Sigma_g^+$, was also studied.

In order to be able to compare present results with those previously reported in Ref. 15 the lowest electronic state found in that work (a $^5\Delta_g$) was added to the previous list. Finally, because an electronic state of $^5\Delta_u$ symmetry was found to lay also rather close to the lowest one in the previous CASCI test calculations it was decided to include it in the set of selected electronic states. This state arises from an $1\sigma_g^2, 2\sigma_g^2, \sigma_u^1, \delta_g^3, \delta_u^4, \pi_u^4, \pi_g^2$, and does not either dissociate into the ground state of the isolated atoms.

TABLE IV. Contribution (percent) of various electronic configurations to the CI wave function of several electronic states of Rh₂. The corresponding weights were obtained through the coefficients of the CI expansion of each electronic state in the $G + M$ subspaces.

	σ_g	σ_u	δ_g	π_u	δ_u	σ_g	π_g	
$^5\Delta_u$								
	2	1	4	4	3	2	2	68%
	2	1	4	3	3	2	3	5%
	1	2	4	2	3	2	4	5%
	1	2	3	3	4	2	3	5%
$^5\Delta_g$ (I)								
	2	1	4	3	4	2	2	72%
	2	1	4	3	3	2	3	3%
	1	2	3	2	4	2	4	2%
	1	2	4	3	3	2	3	2%
$^5\Sigma_g^+$ (I)								
	2	2	4	2	4	2	2	89%
$^5\Delta_g$ (II)								
	2	2	3	3	3	2	3	87%
$^5\Sigma_g^-$								
	2	2	3	3	3	2	3	87%
$^5\Sigma_g^+$ (II)								
	2	2	4	4	2	2	2	60%
	2	2	2	4	4	2	2	18%
	2	2	4	2	2	2	4	2%
	2	2	2	2	4	2	4	3%
$^5\Pi_g$								
	2	2	4	3	3	2	2	67%
	2	2	3	2	4	2	3	20%
$^5\Sigma_g^+$ (III)								
	2	2	3	3	3	2	3	85%
$^5\Phi_g$								
	2	2	4	3	3	2	2	67%
	2	2	3	2	4	2	3	21%
$^1\Sigma_g^+$								
	2	2	4	4	4	2	0	77% at short r and 55% at r_e
	2	2	4	2	4	2	2	10% at short r and 33% at r_e

For each one of the electronic states mentioned above the potential energy curve was obtained using the three-class CIPSI algorithm. The thresholds used to select the G and M subspaces were 0.01 and 0.002, leading, for the quintuplet states, to dimensions of about 50 and 10 000 determinants, respectively. The number of generated determinants was about 2.5×10^6. In the case of the $^1\Sigma_g^+$ electronic state the dimensions are logically greater, being of 93 and 11 000 determinants for the G and M subspaces and including the perturbational second-order contribution of about 4.2×10^6 generated determinants. These values are within the limit of our present computational facilities. At a first sight it may seem that the CI expansions handled in the present work are fairly small. It is then worth pointing out that these are selected CIs obtained from a selected space of references which at present precludes the use of the direct CI approaches. Moreover, it has been recently shown that this approach lead to results close to the full CI benchmarks[31] and it has been able to correctly predict the energy difference between the $^6\Delta$ and the $^4\Delta$ electronic states of FeH.[38]

The CI potential energy curves for these states were always obtained starting from the same set of MOs, namely those arising from a ROHF calculation in the $^5\Sigma_g^+$ ($\pi_g^2 \pi_u^2$). The (5363/3241) basis set (Basis 2) has been used.

Among the different electronic states studied in the present work the stablest one was a $^5\Delta_u$ with a bond mainly of $5s–5s$ character. The calculated spectroscopic parameters for this, as well as for the remaining electronic states, are reported in Table III and the contribution of the more important electronic configurations to each electronic state wavefunction is reported in Table IV. Potential energy curves are reported in Fig. 2.

It is worth pointing out that the predicted ground state of dirhodium found in the present work (a $^5\Delta_u$) is different from the one earlier reported by Balasubramanian and Liao[15] (a $^5\Delta_g$), although the energy difference between them is of only 0.3 eV. These two states correspond formally to bond orders of 2.5 and 3, respectively, although this does not mean that a multiple bond is being formed. The interesting point is that both states involve an excitation from the antibonding combination of the d_σ atomic orbitals to a d_δ molecular orbital, this has the effect of decreasing the Pauli repulsion on the internuclear region where the bond is being formed. Since the electronic repulsion between δ distributions is smaller, these states lie rather low in energy. When dealing with transition metal atoms this argument may be rather naive and, even if it seems a logical explanation, it has to be taken cautiously. For instance, the $^5\Sigma_g^+$ (I) electronic state, which properly dissociates into the ground state of the separated atoms lies only 0.09 eV above the ground state and below the state reported in Ref. 15 as ground state. Hence, this electronic state appears to be the third in the present work.

With respect to results recently reported by Balasubramanian and Liao[15] a few comments are necessary. First, it is worth to point out that among the 30 electronic states studied in Ref. 15 only two (a $^5\Delta_g$, and a $^5\Sigma_g^+$) do coincide with the ones studied here. It is worth pointing out that the $^1\Sigma_g^+$ studied in Ref. 15 is not the same considered in the present
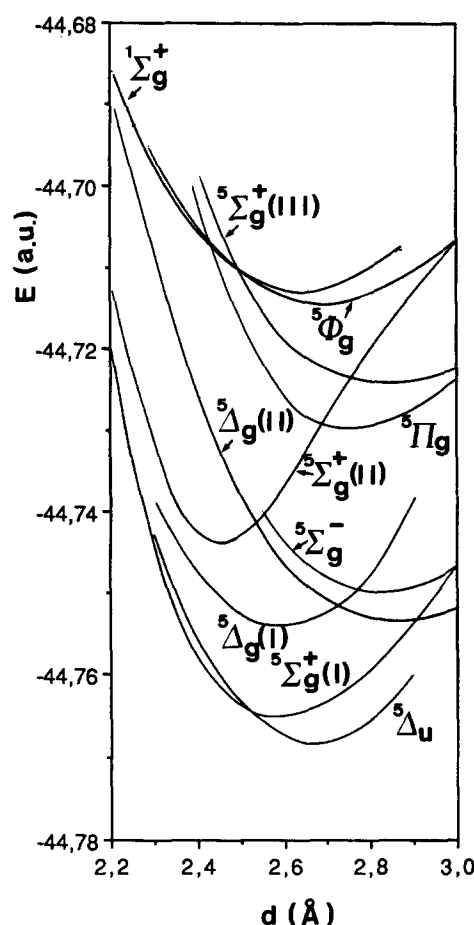

FIG. 2. Potential energy curves for the low-lying states of Rh$_2$.

work. Moreover, all the states studied in the present work lie between those studied in Ref. 15 and were not found as lower roots of the state-averaged CASSCF. This means that by using the procedure described in Ref. 15 there is no guaranty to pick up the lowest electronic states. The present approach does not indeed ensures that this will be the case and it seems that a general recipe does not exist. A second point concerns the description of the wave function corresponding to each electronic state. In Ref. 15 it was found that the leading configurations account for roughly 60% of the total. The present results are somewhat different because, as seen in Table IV, the weight of the leading configuration is, for most of the studied states larger than 80%. For those states coinciding with the ones studied in Ref. 15, the present description fully agrees with that reported by Balasubramanian and Liao. Finally, it is interesting to compare the values for the bonding parameters obtained in Ref. 15 with the present ones. For the $^5\Delta_g$ (I), the ω_e values are in a very good agreement, the r_e value found in the present work is about 0.3 Å larger and it is not clear where the origin of the difference arises, and finally the dissociation energies are quite different, the one reported in Ref. 15 being larger by about 0.9 eV. In this case, part of the difference comes from the way this value is computed in

Ref. 15 and the present value is probably more accurate. With respect to the excited states the same trends are found and an idea about the accuracy achieved in both works is that the energy difference between the $^5\Delta_g$ and the corresponding $^5\Sigma_g^+$ differs only by about 0.4 eV although it is a rather high excited state. Since in the present work each electronic state is treated individually, its corresponding multireference space being iteratively constructed, it is believed that the ordering of the electronic states will not differ substantially by improving the level of calculation, whereas dissociation energies may be more affected by the missing electronic correlation effects.

From the previous discussion it appears that the present results qualitatively agree with those earlier reported in Ref. 15 in spite of the differences in basis sets, pseudopotentials and one-electron functions used to construct the MRCI wave functions. The main differences appear on the energy separation and dissociation energies while the description of the wave function, for those states that do coincide, is quite similar. Because in the present approach there is no *a priori* selection on the multireference space, the resulting CI wave function is more flexible and the results more accurate than those reported in Ref. 15. Since the electronic states described in both works are rather different, both are in fact complementary.

For the ground ($^5\Delta_u$) electronic state the equilibrium internuclear distance is only slightly shorter than the one for bulk Rh. The calculated D_e accounts for roughly 62% of the experimental value[39] and the ω_e is in agreement with the one assumed in Ref. 39 to determine the experimental dissociation energy.

The difference between calculated and experimental value for the dissociation energy indicates how severe the correlation effects are for Rh₂. A point to be stressed is that while bonding in RhH is explained up to 35% at the SCF level, Rh₂ is highly unbound at this level. Moreover, the enormous contribution of correlation energy to the bond formation makes it difficult to have accurate results. Among the 2.10^6 generated determinants, the subset of determinants whose contribution to the electronic correlation is taken variationally (about 10 000) only contributes to a 60% of the total correlation energy, the remaining of which is perturbatively estimated up to second-order. A better estimate of this part would probably improve the present results but at least 500 000 determinants would have to be treated variationally in order to achieve a similar accuracy to that obtained for the RhH molecule. This is still beyond our actual computational facilities although some strategies seem able to make it possible in a near future.[40]

Even after such an improvement, it is not clear how much the present result will be enhanced because on the one hand there is a huge number of determinants to be generated and, on the other hand, it is not clear if electronic correlation arising from $4s^24p^6$ electrons contribution to the bond will be noticeable. Indeed, the number of electronic states studied in the present work is rather limited and the real ground state may not be within the ones studied here.

Likewise, the lack of experimental data makes it difficult to assess how accurate the present values for the excited states are. The only point to be commented is that, among the electronic states studied in this work, the promotion energies are rather high. The lowest excited states being about 0.1 eV higher in energy. The predicted spectrum is then much less dense than the one found by Shim[14] and qualitatively similar to the one derived from the photoelectron spectrum of Co₂.[41]

Finally, $^1\Sigma_g^+$ state will be commented. At the SCF level this state is also unbound although the tendency to form a multiple metal–metal bond is evidenced by the short equilibrium distance found at this level (about 2.11 Å). When CI is carried out, starting from the same MOs as in the study of the quintuplets, the distance is enlarged up to 2.63 Å. It is worth pointing out that the $^1\Sigma_g^+$ electronic state wave function is of rather different physical character at long and short distances. At the former ones the electronic wave function is dominated up to 80% by the closed shell determinant and 10% by the antiferromagnetic coupling of electrons in the π_u^2, π_g^2, configuration, which indeed corresponds to the lowest $^5\Sigma_g^+$ electronic state, which is also the lowest formally dissociating into the ground state of the separated atoms. However, at distances near r_e the CI wave function is dominated only up to 55% for the closed-shell determinant and up to 35% by the π_u^2, π_g^2, one. At larger distances the weight of the closed shell determinant is even smaller. This analysis shows that Rh₂ does not exhibit any important tendency to form metal–metal multiple bonds, at least at the present level of computation. Moreover, $^1\Sigma_g^+$ electronic state is, in energy, the highest one among the ones studied in the present work. It remains slightly unbound at the CI level but missing correlation will probably make it moderately bound.

CONCLUSIONS

The electronic structure of Rh, RhH, and Rh₂ has been studied at the CI level, through the three-class CIPSI algorithm, using nonempirical pseudopotentials and moderately large basis sets.

For the atom itself the energy difference between the two low-lying electronic states is in fairly good agreement with the experimental value. The present value is larger than the one obtained by Langhoff et al.[2] at the CPF level and the accuracy is rather similar to the one found for Fe$^+$[33] and Fe.[38] The differences with respect to the CPF values being mainly due to the inclusion of the $4s^24p^6$ electrons in the valence shell in Ref. 2, while they are in the core in the ECP used here. Since the $4s^24p^6$ electrons have not been correlated in Ref. 2, the improvement with respect to the present value already appears at the SCF level. This is the price to be paid for including the $4s^24p^6$ electrons in the core in order to be able to use a larger basis set in the valence ones. Moreover, the calculated IP and EA are in good agreement (quantitatively and qualitatively, respectively) with experiment. The EA value may surely be improved by optimizing the diffuse functions for Rh⁻ at the CI level. In spite of the limitations discussed above for the description of atomic Rh, results emerging from the present study for RhH are in very good agreement with experiment as well as with the only two previous theoretical studies.[2,17]

In the case of Rh_2, the electronic ground state is found to be a $^5\Delta_u$ at variance with previous studies[14,15] although the physical image of the bond is similar for this state and the one found in Ref. 15. Neither, the present one nor the one reported in Ref. 15 are (at r_e) dominated by an electronic configuration dissociating into the ground state of the separated atoms. Roughly, the present results agree with those reported in Ref. 15 although the electronic states considered in both works are generally different. However, the energy dissociation and energy separations between different electronic states are lower than those previously reported in Ref. 15. Part of the difference in the D_e value comes from the way it is computed in Ref. 15 and part is probably due to the method itself because for RhH, the CASSCF/MRCI of Balasubramanian and Liao the calculated D_e value is 0.3 eV[18] larger than the experimental result.

For the lowest electronic state the calculated D_e is 62% of the experimental value. The origin of the differences between the experimental and calculated data is not clear, for the following reasons: a) Only a few electronic states have been selected. b) The second-order contribution of generated determinants is still too large. c) The set of generator determinants may be improved. d) The error on the EA may be responsible for an unbalanced treatment of left–right correlation due to the incorrect weight of contributions to the electronic wave function. e) The contribution of $4s^2 4p^6$ electrons to the electronic correlation may be important. f) Finally, spin–orbit effects may play an important role.[10,15]

The three first points are of technical character and may be improved in the near future (i.e., starting from a CASSCF calculation will obviously improve somewhat the results and the use of approximate natural orbitals will help to enhance the convergence of the CI expansion [see Ref. 31(b)]. The three last ones are, however, more subtle because, in order to achieve some improvement, the basis set has to be enlarged and this fact will have repercussions on the former points.

The present results for Rh_2 should then be taken cautiously although they are believed to be correct, at least qualitatively. With respect to the possibility of a multiple metal–metal bond in Rh_2, the present study shows that magnetic effects predominate over the bonding ones and makes the $^5\Sigma_g^+$ state more stable than the $^1\Sigma_g^+$. Moreover, at r_e the electronic wave function corresponding to $^1\Sigma_g^+$ is a mixture of the closed shell and the $\pi_u^2\,\pi_g^2$ configurations the latter being, in the antiferromagnetic coupling, the dominating configuration in the $^1\Sigma_g^+$ electronic state. However, the quintuplets properly dissociating into the ground state of the separated atoms have a too large repulsion in the internuclear region and the consequence is that the electronic ground state is dominated (at r_e) by an electronic configuration that does not correlate with the atomic ground state limit.

ACKNOWLEDGMENTS

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