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Model potential calculations for second-row transition metal molecules within the local-spin-density method

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The model potential (MP) method originally proposed by Huzinaga and Bonifacic is extended to spin-polarized local-spin-density calculations, including scalar relativistic effects. The theoretical justification of the MP method in this case is studied and the method of optimization of the basis functions and MP parameters is given. The validity of the frozen core approximation is studied for Mo_2, Ru_2, and Ag_2. It is found that the MP can very accurately reproduce all-electron (AE) results if the $4p$ electrons of Ag and the $3d$ electrons of Mo are also considered as valence electrons, although inclusion of these electrons in the core still yields a useful level of accuracy. It is shown that the present MP results are not sensitive to basis set superposition errors (BSSE). Upon inclusion of the scalar relativistic effects the calculated bond length and vibrational frequency of Ag_2 are in near perfect agreement with experiment, while the dissociation energy is overestimated by 23% with the "best" local potential (VWN). MP calculations have also been performed for AgH, AgO, and AgF. The same level of agreement with experiment as for Ag_2 was found, with the exception of the bond length for AgO. Our calculated bond length is 0.05 Å shorter than the presently accepted experimental value. Since some uncertainty is associated with the spectroscopic assignments for AgO we believe an experimental reexamination would be in order.

I. INTRODUCTION

The local-spin-density (LSD) method has proven[1–3] to be a very useful tool for the description of the electronic structure of various molecules containing transition metal atoms. To extend the scope of this method to the treatment of large clusters containing transition metal atoms, which is a necessary step in understanding complex chemisorption and catalytic phenomena, there is a need for simplification of the LSD calculations. One of the obvious ways is to take into account only the valence electrons of the cluster, assuming they move in an unchanging potential due to the atomic core electrons. Assuming that the frozen-core approximation is valid, a number of different pseudopotential methods have recently been proposed within both Hartree–Fock[4,5] and LSD[6–8] approaches.

The ultimate goal of the pseudopotential methods is to represent the valence orbitals using truncated basis sets and to replace operators of the core-valence interaction by simple, preferably one-electron, analytical potentials. However, the truncation of the valence basis set can seriously affect the description of the valence–valence and valence–core interactions, which requires the introduction of corrections into the analytical potentials as is usually done in atomic calculations. In the case of very distorted (nodeless) valence orbitals these corrections are large and may result in an incorrect description of the interorbital interactions.[9] The basis set superposition error (BSSE) which can be large in pseudopotential calculations with a "soft" inner part of the valence orbitals should also be of concern.[10] Applying a proper (with nodes) valence basis set, which is possible with the model potential method (MP) originally proposed by Huzinaga and Bonifacic,[11] one should in principle closely reproduce all-

electron (AE) results[5] provided that the valence basis set is sufficiently large (to maintain orthogonality with core orbitals) and that core–valence interactions are correctly described.

In the present paper, Huzinaga-type model potentials are developed for the spin-polarized local-spin-density method. So far, MP has been applied in the spin-nonpolarized HFS-$X\alpha$ scheme by Katsuki *et al.*[8] In that treatment the full, untruncated basis set was used. In the present paper a new scheme of MP optimization is introduced which allows correct atomic results to be obtained with profoundly truncated valence basis sets when the inner-core like model potential parameters are properly optimized.

In the first part of the paper the theoretical justification of the MP scheme in spin-polarized calculations is examined. Then the method of choosing the model potential parameters and basis sets is discussed. A straightforward interpolation formula for the MP parameters and basis sets of both spins is found to be satisfactory.

The central assumption in any pseudopotential approach, the frozen-core approximation, has been carefully examined. It is found that the size of the valence space has to be increased to account for changes in spin polarization of the core if there is a large difference between the isolated atom and the atom in the molecule. In the case of Ag_2 the inclusion of the $4p$ electrons in the valence shell along with $5s$ and $4d$ yields near perfect agreement with the results of all-electron calculations, whereas for Mo_2 electrons from $3d$ up have to be treated explicitly to obtain highly accurate results.

Since relativistic effects are known to significantly influence the bonding in molecules containing second-row transition atoms, the approximate treatment of the mass–velocity and Darwin terms was incorporated into the model potential parameters in essentially the same way as was done by Kahn *et al.*[12] and by Klobukowski.[13]

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Upon inclusion of the relativistic effects the bond length and vibrational frequency of Ag_2 turned out to be very close to the experimental data, thus demonstrating that the LSD method is capable of providing a correct description of the potential curves, at least in the vicinity of the minimum, for second-row transition molecules as well as for first-row molecules.[1,2] In the case of Mo_2 the large discrepancy between experiment and a previous pseudopotential study[14] is largely removed in the present MP calculation.

One of the aims of the present study is to find economical representations of the MP for Ag, which will be used later in chemisorption calculations on silver clusters.[15] A considerably truncated and then contracted valence basis set has been proposed and applied to calculations on various molecules containing the Ag atom: AgH, AgO, AgF. Upon inclusion of relativity the equilibrium bonding properties are close to experiment for AgH and AgF. For AgO our calculated equilibrium distance is 0.05 Å shorter than the presently accepted experimental value. We believe that the accuracy of our LSD MP is sufficient to suggest that an experimental reexamination would be in order.

The BSSE which can significantly affect calculated bonding properties whenever small or medium size basis sets are used[16] is shown to be negligibly small in the present MP approach.

II. THE MP METHOD IN LSD CALCULATIONS

Using Hermitian coupling operators[17] Höjer and Chung[18] have shown that the MP method of Huzinaga and Bonifacic[11] is exact in the case of *closed-shell* HF systems. Applying the same kind of technique it is easy to show that the MP method is also correct for the LSD approach, including the spin-polarized (unrestricted) case.

The Kohn–Sham equations for a spin-polarized system of N electrons are as follows:

$$F^\sigma \psi_i^\sigma = \sum_j \epsilon_{ij}^\sigma \psi_j^\sigma, \quad \sigma = +, -, \tag{1}$$

$$F^\sigma(\mathbf{r}) = h(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[n_+(\mathbf{r}), n_-(\mathbf{r})], \tag{2}$$

where n_+ and n_- denote the spin-up and spin-down densities, $n = n_+ + n_-$, v_{xc} represents the exchange-correlation potential, and

$$h(\mathbf{r}) = -\tfrac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_I}.$$

The density n_σ is defined in terms of molecular orbitals ψ_i^σ:

$$n_\sigma(\mathbf{r}) = \sum_i f_i^\sigma |\psi_i^\sigma(\mathbf{r})|^2, \tag{3}$$

where f_i^σ is an occupation number.

Now the set of molecular orbitals can be separated into valence (v) and core (c) manifolds. Assuming orthogonality between valence and core orbitals one can transform Eq. (1) into

$$(F^\sigma - P^\sigma F^\sigma)\psi_i^\sigma = \sum_j^v \epsilon_{ij}^\sigma \psi_j^\sigma, \tag{4}$$

where P^σ is a projection operator

$$P^\sigma = \sum_c |\psi_c^\sigma\rangle\langle\psi_c^\sigma|. \tag{5}$$

After symmetrization of Eq. (4) one can find a unitary transformation which brings it to diagonal form:

$$(F^\sigma - P^\sigma F^\sigma - F^\sigma P^\sigma)\psi_v^\sigma = \epsilon_v^\sigma \psi_v^\sigma. \tag{6}$$

Since the operator F^σ is the same for both core and valence orbitals of spin σ Eq. (6) finally can be written as

$$(F^\sigma - \sum_c 2\epsilon_c^\sigma |\psi_c^\sigma\rangle\langle\psi_c^\sigma|)\psi_v^\sigma = \epsilon_v^\sigma \psi_v^\sigma. \tag{7}$$

A similar equation is valid for closed-shell Hartree–Fock systems; however, for the usual (restricted) open-shell HF method, additional coupling operators enter[18] Eq. (7) and their treatment inevitably involves further approximations. The effects of the coupling operators are "absorbed" by the model potential parameters. In the LSD method, restricted or unrestricted, no such coupling operators appear, so that, if no further approximations are made, Eq. (7) is exact. One can separate F^σ into a valence part (F_v^σ) and a model potential (V_{MP}^σ) operator

$$F^\sigma = F_v^\sigma + V_{MP}^\sigma, \tag{8}$$

where

$$F_v^\sigma(\mathbf{r}) = -\tfrac{1}{2}\nabla^2 - \sum_I \frac{Z_I^v}{r_I} + \int \frac{n_v(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n_{+v}, n_{-v}]$$

and

$$V_{MP}^\sigma = F^\sigma - F_v^\sigma. \tag{9}$$

The V_{MP}^σ can be further divided into contributions from particular atoms assuming that core orbitals do not overlap with each other and that cross terms in the exchange and correlation potentials can be disregarded.

$$V_{MP}^\sigma = \sum_I V_{MP,I}^\sigma, \tag{10}$$

where

$$V_{MP,I}^\sigma = \frac{-Z_c^I}{r_I} + \int \frac{n_c^I(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n_{+c}^I, n_{-c}^I]. \tag{11}$$

III. PARAMETRIZATION OF THE MP EQUATION

To make the MP scheme a workable tool for studying large clusters of atoms we have to introduce approximations to represent V_{MP}^σ, core and valence orbitals in the simplest possible manner which maintains the physical sense of our MP approach.

First a single (common for both spins) model potential V_{MP} is introduced by applying the simple interpolation formula

$$V_{MP} = \tfrac{1}{2}(V_{MP}^+ + V_{MP}^-). \tag{12}$$

This, of course, introduces errors in the exchange correlation potential. However, even for the Mo atom, where the polarization is large, the differences between the potentials are reasonably small (Fig. 1). The largest absolute discrepancies
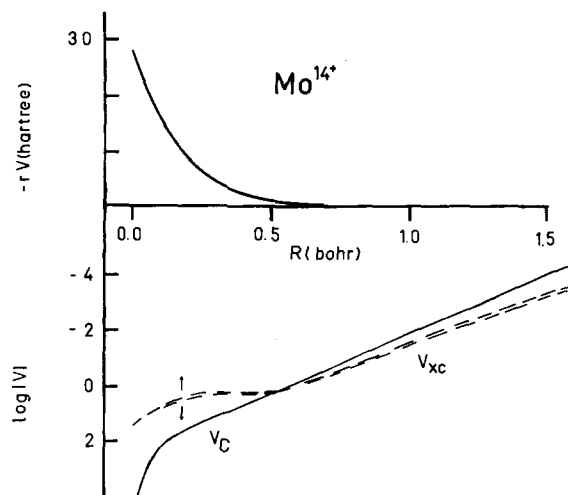
FIG. 1. Total model potential [Eq. (12)] V, Coulomb potential V_c, and exchange-correlation potentials V_{xc} for spin $\alpha(\uparrow)$ and $\beta(\downarrow)$ for the Mo atom with $4s$, $4p$, $4d$, and $5s$ valence electrons.

occur in the inner part of the potential but here the Coulomb potential dominates V_{MP} and after all that whole part of the potential will be changed during the optimization process (see below). The possibility of using the total (core + valence) exchange-correlation potential in MP [Eq. (7)], which makes V_{MP} insensitive to the spin distribution[19] was not considered here since it would increase the size of the auxiliary set used to fit V_{xc} and consequently it is computationally more demanding.

As can be seen from Fig. 1 the total V_{MP} can be well represented as

$$V_{MP}(r) = \sum_k A_k \frac{\exp(-\alpha_k r^2)}{r} \qquad (13)$$

with the constraint

$$\sum_k A_k = N_c, \qquad (14)$$

where N_c is the number of core electrons.

A similar analytical expression was used by Katsuki et al.[8] $V_{MP}(r)$ was numerically generated from numerical radial atomic orbitals obtained using a SW-LSD-VWN program[20,21] adapted for atomic calculations. In the case of relativistic calculations, the reference atomic orbitals were obtained from Cowan–Griffin (Wood–Boring)-type LSD–VWN atomic calculations.[22]

The core orbitals for the projection operator of Eq. (7) are approximated by a least squares fit (LSF) procedure using an even tempered expansion common for all orbitals of the same symmetry. For example, if $\psi_c (c = 1s,2s,3s)$ orbitals of the Ag atom represent the core, they are fitted to a single set of $1s$-type normalized Gaussian functions f_i:

$$\tilde{\psi}_c = \sum_i a_{ci} f_i, \qquad (15)$$

chosen to minimize the error Δ,

$$\Delta = \sum_c \sum_{\text{mesh}} [\psi_c(r_m) - \tilde{\psi}_c(r_m)]^2 r_m^2. \qquad (16)$$

The linear parameters are obtained from the condition

$$\delta\Delta/\delta a_{ci} = 0. \qquad (17)$$

Since we are using a rather small number of functions f_i, it turned out to be advantageous to introduce additional orthonormalization conditions to Eq. (16) in the usual way, through Lagrangian multipliers. In this manner our ψ_c functions are orthonormal among themselves and they are also orthogonal to the valence orbitals. Hence, they closely resemble the true core atomic orbitals of Eq. (7). Similarly as in the case of the model potential [Eq. (12)], the core orbitals for both spins are represented by one set, averaged over the spins. Finally, the valence orbitals were prepared using an LSF procedure in essentially the same way as described above [Eqs. (15) and (16)]. In that case the even-tempered constraint was not imposed and the orthogonality to core orbitals was not forced.

Once the LSF parameters have been obtained for the case of a considerably truncated valence basis set, it is necessary to adjust the MP parameters to restore the reference (ref) valence properties of the atom. Unlike in the HF-type optimization where the presence of the nonlocal exchange potential modeled by a local model potential forces quite pronounced reoptimization of the MP parameters, the LSD potential is local and in principle no adjustment of MP parameters (obtained in the LSF stage) is necessary as long as the full valence basis set is employed. The valence basis set employed here is limited in the inner part of the valence orbitals; thus it seems to be reasonable to optimize the corresponding inner-core like part of the MP, while leaving the long-range (outercore) part of the MP unchanged after the LSF stage. Instead of introducing an inner and an outer core model potential (which would double the number of MP parameters) the $V_{MP}(r)$ from Eq. (13) was split into inner, V_{MP}^i (with large α_k) and outer, V_{MP}^o (small α_k) parts. Both linear A_k and nonlinear α_k parameters of V_{MP}^i are optimized. To maintain the asymptotic properties of V_{MP} the optimized linear parameters (A_k') were normalized to those of the LSF (A_k):

$$\sum_k^i A_k' = \sum_k^i A_k. \qquad (18)$$

The optimization was carried out by extending the procedure given by Sakai[23] by adding the term (Δ_0) which forces orthogonality between valence and core orbitals. Thus we minimized the sum of deviations:

$$\Delta = \Delta_\epsilon + \Delta_f + \Delta_0, \qquad (19)$$

where

$$\Delta_\epsilon = \sum_v w_v^\epsilon |\epsilon_v^{\text{ref}} - \epsilon_v|, \qquad (20)$$

$$\Delta_f = \sum_v w_v^f \sum_{\text{mesh}} \{[\psi_v^{\text{ref}}(r_m) - \psi_v(r_m)]/\psi_v^{\text{ref}}(r_m)\}^2, \qquad (21)$$

and

$$\Delta_0 = \sum_v w_v^0 \sum_c \langle \psi_v | \psi_c \rangle^2. \qquad (22)$$

The weights w_v were chosen to provide comparable errors in the properties of valence orbitals.

TABLE I. The MP data for Ag including scalar relativity. A. MP parameters [Eq. (13)] after LSF stage and after atomic optimization. B. Atomic core orbitals and values of $2\epsilon_c$ of Eq. (7). C. Valence orbitals and contraction scheme [4,4,3]. In molecular calculations a $5p$-like polarization function was added with exponent 0.05.

A.

	LSF parameters		Optimized parameters	
	α	c	α	c
	3089.2	− 4.4963	1157.5	− 6.5666
	261.63	− 6.6039	231.77	− 2.3120
	36.309	− 10.590	30.300	− 12.8120
	7.2730	− 7.2860	7.2730	− 7.2860
	1.8372	− 0.9380	1.8372	− 0.9380
	0.7851	− 0.0853	0.7851	− 0.0853

B. s-type core orbitals

α	$1s$	$2s$	$3s$	$4s$
0.9066	− 0.0112	0.0082	− 0.0473	− 1.1048
2.8371	− 0.0071	− 0.0405	0.3708	− 0.0662
8.8781	0.0298	0.0596	1.0908	1.0290
27.782	− 0.0263	− 0.7657	− 0.7218	− 0.4301
86.937	0.0522	− 0.4724	− 0.3472	− 0.1450
272.05	0.4118	0.3059	0.1630	0.0630
851.32	0.4632	0.1946	0.0841	0.0401
2663.9	0.1471	0.0609	0.0285	0.0114
8336.3	0.0863	0.0291	0.0124	0.0056
$- 2\epsilon_c$:	1851.6	272.94	49.996	6.9527

p-type core orbitals

α	$2p$	$3p$
5.1443	0.0009	− 0.5759
15.036	0.0066	− 0.5896
43.945	0.4927	0.2252
128.44	0.4539	0.2332
375.50	0.1302	0.0633
1097.2	0.0427	0.0195
$- 2\epsilon_c$:	245.85	40.963

d-type core orbital

α	$3d$
4.4672	0.3179
13.824	0.5933
42.777	0.2725
132.37	0.0587
$- 2\epsilon_c$:	26.385

C. Valence orbitals

$5s$		$4p$	
α	c	α	c
852.74	− 0.0146	139.97	0.1316
41.344	0.0978	9.9520	− 0.4671
7.4714	− 0.2731	1.6691	0.6922
1.0761	0.5592	0.6070	0.4329
0.1079	− 0.7586		
0.0390	− 0.3774		

$4d$	
α	c
25.629	− 0.2179
1.5619	0.5734
0.4249	0.5221
0.0900	0.1202

IV. ATOMIC MODEL POTENTIAL CALCULATIONS

Applying the method described in Sec. II, atomic MP have been optimized for Ag, Mo, and Ru. The parameters and basis sets for a Ag^{17+} MP which explicitly includes $5s$, $4d$, and $4p$ electrons in the valence shell are given in Table I. The data for MP calculations of other atoms are available on request.

TABLE II. The valence atomic orbital energies (ϵ_v) obtained from MP atomic calculations in comparison with reference (numerical) orbital energies (ϵ_v^{ref}). The errors $\Delta = \epsilon_v^{ref} - \epsilon_v$ are given (in eV) for various MP after LSF stage (LSF), and after optimization (OPT). Blank entries are less than 0.1 eV.

		↑:5s	4d	4p	4s	↓:5s	4d	4p	4s
Nonrelativistic calculations									
Ag^{19+}	LSF			0.4	−0.1		0.1	0.4	−0.1
Ag^{19+}	OPT		0.1				0.1		
Mo^{14+}	LSF		0.1	0.3	−0.1			0.1	−0.5
Mo^{14+}	OPT		0.1	0.1					−0.1
Ru^{16+}	LSF	0.1	0.1	0.4	−0.1		0.1	−0.1	−0.4
Ru^{16+}	OPT		0.1	0.1			0.1		
Relativistic calculations									
Ag^{19+}	LSF		0.3	−1.5	0.8		0.3	−1.5	0.8
Ag^{19+}	OPT		0.1		0.6		0.1	0.1	0.6
Ag^{17+}	LSF	0.2	0.3	−0.5		0.2	0.2	0.5	
Ag^{17+}	OPT	0.1	0.1			0.1	0.1		
Mo^{14+}	LSF		−0.2	−0.7	0.1		−1.1	−0.3	
Mo^{14+}	OPT		0.1	0.3	0.2		0.2	0.4	

In Table II the performance of the MP in atomic calculations is displayed. The errors in valence orbital energies are already rather small after the LSF stage and they can be further diminished after a few optimization [see Eq. (19)] cycles. The errors from relativistic calculations are somewhat larger than those from nonrelativistic ones, especially if the valence space is enlarged and includes 4s electrons. This is a consequence of difficulties in modeling the direct relativistic effects through local model potential parameters. The shape of the valence orbitals is improved slightly after optimization is done and, in all cases considered, the outermost part of the valence orbitals (outside the last node) is precisely reproduced using the present MP, whereas the inner part is of lesser accuracy. In Fig. 2 the 4p, 4d, and 5s orbitals from a Ag^{17+} MP are displayed and compared with the reference orbitals. The overlap of valence and core orbitals improves along with the orbital shapes during optimization and in all cases considered does not exceed 10^{-2}.

V. MOLECULAR MODEL POTENTIAL CALCULATIONS

Molecular model potential calculations have been performed using a modified version of Dunlap's LCAO-$X\alpha$ program.[24] The limited valence space in the case of MP calculations allows us to use a small set of auxiliary functions, thus significantly improving the performance of the program. The auxiliary sets for both density and exchange correlation potentials were prepared using a recently described method.[16] The full valence space was used in optimization of the s part of the auxiliary sets, whereas 4d and 5s orbitals only serve for fitting of the polarization auxiliary sets of d and p type. The auxiliary sets are available on request. We estimate that for Ag_2 calculations with the Ag^{17+}MP and (7,3,4/7,3,4) (7s, 3p, and 4d Gaussian-type auxiliary functions for density and exchange-correlation fits) auxiliary sets, the CPU time with the present version of the program was reduced almost four times in comparison with that for all electron calculations. Equally important is the reduction in core memory for the storage of the auxiliary function matrices.

A. Test of the frozen core approximation

The central approximation of any pseudopotential scheme, the frozen core approximation, is tested here in calculations for Mo_2, Ru_2, and Ag_2 using a nonrelativistic model potential. In Table III the calculated molecular properties are presented and compared with the results of all-electron (AE) calculations.

The AE calculations for Ru_2 and Ag_2 were done using compact basis sets[16] of the type $(432221/4221^*/4211^+)$. In the case of Mo_2 comparison is made with the results obtained
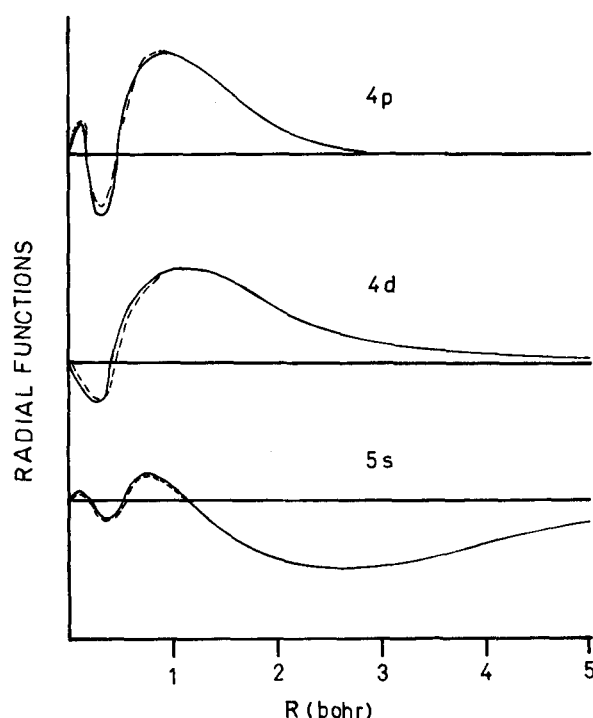

FIG. 2. Radial core functions multiplied by r for the 4p, 4d, and 5s orbitals of Ag with model potential; (solid curve) in comparison with reference orbitals (broken curve).

TABLE III. Test of the frozen core approximation (nonrelativistic calculations).

	R_e(Å)	D_e(eV)	ω_e(cm^{-1})
Ag$_2$($^1\Sigma$)			
AE[a]	2.53	2.4	219
AE–BSSE	2.55	2.0	195
MP(4s)[b]	2.55	2.0	173
MP(4p)	2.56	2.0	202
Mo$_2$($^1\Sigma$)			
ext AE[c]	1.97	5.0	423
MP(4s)	2.02	4.3	490
MP(3d)	1.98	4.8	479
Ru$_2$($^7\Sigma$)			
AE[a]	2.41	2.7	380
MP(4s)	2.42	3.0	330

[a] All-electron calculations using (432221)/4221*/4211$^+$) (Ref. 16) basis set.
[b] The first valence shell of the atom is marked in parentheses.
[c] Extended basis set calculations taken from Ref. 2.

using an extended basis set.[2] It is seen from Table III that a larger valence space has to be used for Mo$_2$ than for Ag$_2$ calculations to closely reproduce the AE results. In the case of Ag the MP has to treat 4p electrons as part of the valence shell whereas, for Mo, 3d electrons have to be treated explicitly if very high accuracy is desired. This does not mean that these outer core electrons take part in the bond, but rather that the present MP scheme is unable to treat them as frozen core electrons.

Especially in the case of Mo$_2$, the core electrons in the atom and in the molecule have different spin polarization and that change cannot be accurately reproduced in the present MP approach, unless a relatively small core is considered. The present method forces orthogonality of the valence and core orbitals. When the core orbitals change their spin polarization in the molecular environment then overlap contributions between core and valence orbitals occur and deform the description of the valence molecular orbitals. The possibility of diminishing the core–valence overlap constraint by making the $2\epsilon_k$ coefficient in Eq. (7) smaller, as suggested by Gropen et al.,[25] was however ruled out since it has little theoretical justification and it makes the description of the atom unsatisfactory. The necessity of using the relatively larger valence space seems to be a general feature of this kind of MP and was also found in Hartree–Fock calculations.[13]

Judging from the orbital energies, the bond in Ag$_2$ can be described as the interaction of the 5s electrons coupled with 4d electrons with a small contribution coming from 4p. In the case of Mo$_2$ there are significant changes in 4s and 4p orbital energies upon formation of the molecule, thus showing that here the outer core electrons are involved in the bond. This last observation may explain the relatively large discrepancy (0.17 Å) with experiment found in a previous pseudopotential calculation of the bond length in Mo$_2$.[14]

It is known that basis set dependent calculations like LCAO–LSD are influenced by the basis set superposition error (BSSE) if the basis set is not extensive enough.[16] In fact, for Ag$_2$, this effect is quite significant for the binding energy

(see Table III). It should be expected that a model potential scheme which eliminates core-like electrons can significantly reduce the BSSE.[10] In a previous paper,[16] we pointed out that BSSE can be uniquely defined in LCAO–LSD calculations using the counterpoise method.[26] Applying that method here, the results of AE calculations corrected for BSSE are compared in Table III with MP results. The agreement is almost perfect, thus demonstrating that the method of correction for BSSE is sound. The direct calculation of BSSE in the present MP calculations shows the effect to be negligible (less than 0.05 eV for Ag$_2$).

B. Calculations for Ag$_2$, AgH, AgO, AgF

Using a relativistic MP (Ag^{19+} and Ag^{17+}) and a nonrelativistic one (Ag^{19+}), molecular calculations for Ag$_2$, AgH, AgO, and AgF have been performed. In Table IV comparisons are made with experimental data and with the results of other authors.

First, one can see that the Ag^{17+} MP with a considerably reduced basis set (see Table I) provides the same molecular results as the more extended Ag^{19+}MP with a larger basis set. Thus the present results are saturated with respect to the quality of the basis set and model potential. Comparison with experiment reveals excellent agreement for relativistic MP results for the bond distances of all the molecules except for AgO which is somewhat worse. Taking into account that the polarity of the AgO bond should be similar to (or somewhat less) than that in AgF and that in the latter case good agreement with experiment was found, we suspect that the experimental value of R_e may be incorrect for AgO. In fact, inspection of the literature[27,33] shows that there is some uncertainty about the assignment of the ground state. The calculations on AgO and AgF were done at the same level of accuracy (the same quality of basis set, MP parameters, etc.). The orbital energies for both AgO and AgF reveal that the same type of silver orbitals take part in the bond (5s, 4d, 4p, and partly 4s), so we cannot explain the difference in comparison with experiment otherwise than to invoke an incorrect experimental result.

The dissociation energy is consistently overestimated, especially for AgO and AgF. The main reason for this seems to be the incorrect estimation of the electron affinity of the O and F atoms. In the present LSD-VWN approach the electron affinity is too large by 0.7 eV for O and by 0.8 eV for F in comparison with the experimental values. Similar problems were encountered in CI calculations for oxides.[32] The simplest remedy for this involves the use of the experimental value of the electron affinity (or even the ionization potential) instead of the calculated ones. Incorporation of this correction into the present model results in very good agreement of the calculated and experimental binding energies.

The vibrational properties of the silver compounds are in acceptable accord with experiment (10%). Comparison of relativistic and nonrelativistic results shows that contraction of the bond takes place upon including relativity, in line with the findings of other authors.[13,28,31] However, our contraction is much smaller than that found previously by Ziegler et al.[28] and is closer to that found in the Dirac–Hartree–Fock calculations on AgH by Lee and McLean.[31]

TABLE IV. Molecular relativistic (R) and nonrelativistic (N) results for Ag_2, AgH, AgO, and AgF.

		R_e(Å)		D_e(eV)		ω_e(cm^{-1})
$Ag_2(^1\Sigma)$						
Experiment[a]		2.47		1.7		192
Ziegler[b]	R	2.52		2.0		203
	N	2.67		1.7		184
Martins[c]	R	2.51		2.2		212
Stoll[d]	R	2.55		1.8		186
	N	2.66		1.7		165
Present MPI[e]	R	2.48		2.1		186
	N	2.55		2.0		172
MPII[f]	R	2.50		2.1		214
$AgH(^1\Sigma)$						
Experiment[a]		1.62		2.4		1760
Ziegler[b]	R	1.61		2.0		1709
	N	1.71		1.7		1605
Stoll[d]	R	1.74		2.0		1616
McLean[g]	R(R')	1.70	(1.62)	1.3	(2.3)	
	N	1.77		1.2		
Present MPI[e]	R	1.61		2.9		1850
	N	1.65		2.7		1790
MPII[f]	R	1.61		2.9		1870
$AgO(^2\Pi)$						
Experiment[a]		2.00		2.2		490
Stoll[h]		2.17		1.9[h]		462
Present MPI[e]	R	1.94		3.1	(2.4)[h]	560
	N	1.99		3.0		518
MPII[f]	R	1.95		3.0		552
MPIII[i]	R	1.96		2.8		535
$AgF(^1\Sigma)$						
Experiment[a]		1.98		3.6		513
Present MPI[e]	R	1.97		4.4	(3.6)[h]	584
	N	2.01		4.4		548
MPII[f]	R	1.97		4.3		580

[a] Reference 27.
[b] Reference 28, DVM method employed with pseudopotential Ag^{11+}.
[c] Reference 29, LCAO–LSD pseudopotential (Ref. 7) Ag^{11+} used with [3,3,4] basis set.
[d] Reference 30, semiempirical pseudopotential Ag^{1+} with [8,5,3] basis set.
[e] Present MP Ag^{19+} with (8,7,5) basis set contracted to [6,5,4].
[f] Present MP Ag^{17+} with (6,5,4) basis set contracted to [4,4,3].
[g] Reference 31, Dirac–Hartree Fock calculations; results obtained with nonrelativistic estimation of the correlation energy are given in parentheses.
[h] Reference 32, in the calculations by Stoll et al. the binding energy of AgO is calculated first with respect to Ag and O^- and subsequently the experimental value of the electron affinity for the O atom is used. This procedure employed in the present LSD approach also considerably improves the binding energy.
[i] Present MP Ag^{17+} with (6,5,4) basis set contracted to [3,2,1] and with auxiliary set (5,1,2/5,1,2).

The sensitivity of the MP results to the contraction of the orbital basis set was checked for the case of AgO. The basis set from Table I was contracted to the [3, 2, 1] level and supplemented with a very reduced auxiliary set (5,1,2/5,1,2) (both sets are available on request). The results given in Table IV are virtually unchanged by this contraction.

VI. CONCLUSION

The model potential method has been extended to treat spin-polarized LSD–VWN molecules containing second-row transition metals. The inclusion of scalar relativistic corrections yields excellent agreement with experiment for the geometries of the molecules investigated, with the exception of AgO. Here we expect that new experiments may correct the bond length. Since the vibrational properties are

acceptable and the binding energy is consistently too large by $\sim 30\%$, we believe the present method represents a very useful tool for investigation of larger clusters composed of transition metals.

Although the present MP approach is more expensive than other (nodeless) pseudopotentials,[7] it has the advantage that the results can be systematically improved by improving the basis set or, if necessary, by expanding the valence shell. Indeed, in the case of Mo_2 it was necessary to include the $3d$ orbitals in the valence shell to obtain very accurate results. We attribute the problems when a small space is used to breakdown of the frozen core approximation brought about by the condition of orthogonality between core and valence orbitals which is particularly severe when a large change in spin polarization takes place upon formation of the molecule. Clearly, there is a need for introduction into the present

MP scheme of a correction to allow for electrostatic[30,32] and spin polarization of the core.

In the case of Ag the model potential Ag^{17+} with a (6, 5, 4) Gaussian basis set contracted to [4, 4, 3] or even to [3, 2, 1] is found to be BSSE free and yields very accurate molecular results for various molecular environments. Although it is more expensive than other (nodeless) pseudopotentials[7] we can recommend it as a very reliable pseudopotential.

When the present work was completed, papers by Hay and Wadt[34] appeared with newly generated *ab initio* effective core potentials for most atoms. The authors recommend the explicit inclusion of the outermost core orbitals in the valence space, especially for correlated treatments of transition metal compounds. The nodal structure of the valence orbitals seems to be important for the proper account of correlation. Results of the present paper fully support this conclusion. Taking into account that the innermost part of the valence orbitals in our treatment may be effectively contracted, the size of the orbital basis set (at the SCF level) is now comparable with that from Ref. 34, so that the "gap" in basis set demands between model potentials and effective core potentials is considerably diminished.

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