Pseudopotential approaches to Ca, Sr, and Ba hydrides. Why are some alkaline earth MX₂ compounds bent?

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Quasirelativistic and nonrelativistic 10-valence-electron pseudopotentials for Ca, Sr, and Ba are presented. Results of calculations with 6s6p5d basis sets for MH, MH⁺, and MH₂ are compared with all-electron and 2-valence-electron pseudopotential calculations with and without core-polarization potentials. The 10-valence-electron pseudopotential approach agrees well with all-electron calculations. It circumvents problems for the 2-valence-electron pseudopotentials arising from an incomplete separation of valence and subvalence shells in polar molecular systems due to strongly contracted occupied (n – 1)-d orbitals. All higher-level calculations show SrH₂ and BaH₂ to be bent with angles of ~140° and 120°, respectively, while CaH₂ is linear with a flat potential-energy surface for the bending motion. The use of a core-polarization potential together with the 2-valence-electron pseudopotential approach allows an investigation of the relative importance of core-polarization vs direct d-orbital bonding participation as reasons for the bent structures. The calculations strongly suggest that both contribute to the bending in SrH₂ and BaH₂. Even at the Hartree–Fock level of theory 10-valence-electron pseudopotential calculations given reasonable angles when the potential-energy surface is not exceedingly flat, and only moderately contracted basis sets including both compact d functions and diffuse p functions are used. The effect of core-valence correlation and the importance of f functions also are discussed.

I. INTRODUCTION

The bent structures of some MX₂ compounds of the heavier alkaline earth metals are still considered to be unsolved problems.¹

In 1963–1964 the electric-quadrupole deflection experiments of Klemperer and co-workers indicated that some of the dihalides of group 2 had bent thermal average structures.² Since then there have been both experimental³ and theoretical⁴ efforts to verify and find straightforward explanations for these results, which contradict simple bonding models.⁵ Since then there have been both experimental⁶ and theoretical⁷ efforts to verify and find straightforward explanations for these results, which contradict simple bonding models [e.g., the valence shell electron pair repulsion (VSEPR) model,⁸ Walsh diagrams,⁹ or simple ionic, MO, and valence-bond pictures].

Recently, gas-phase electron-diffraction studies of MCP₅ molecules (Cp* = Me₅Cp) indicated that these phenomena would be of general importance in the emerging field of Ca-, Sr-, and Ba-organometallic chemistry.⁷

The models are employed to explain the energy gain for bent structures. The participation of d orbitals in the covalent contribution to the bonding was proposed by Hayes.¹⁰ The alternative model emphasizes the polarization of the large M + ² cations by the anions as being the main driving force for the bending.¹¹ While the present work was in progress, v. Szentpály and Schwerdtfeger¹² argued that the M + ² core polarization was not large enough to explain the bent structures. They proposed a model based on the difference in atomic softness¹³ between metal and substituents. When this difference is larger than a certain value, the molecule is predicted to be bent, otherwise it should be linear.¹⁴

Ab initio quantum-chemical calculations that might shed light on the problem usually focused on CaF₂,¹⁵ which has an extremely flat potential-energy surface for the bending motion. The use of increasingly flexible basis sets does not necessarily give smooth convergence towards either linear or bent geometries. Even the highest levels of theory used previously¹⁶ do not establish whether the equilibrium geometry of CaF₂ is bent or linear. Therefore, CaF₂ is not the best choice to probe the effects responsible for the bent structures. The necessity of using high-level all-electron calculations has prevented an examination of Sr and Ba compounds, which might be easier to analyze.

A 2-valence-electron pseudopotential (or effective core potential, designated 2-ve-ECP) treatment would be much less expensive computationally, but suffers from an incomplete separation of valence and subvalence shells.¹⁷ The (n – 1)-d orbitals are occupied in molecular systems with significant positive charge on the metal (particularly for the heavier elements) and extend far into the region of the (n – 1)-s and p orbitals.¹⁸ A clear-cut separation between valence space and these orbitals is difficult to achieve. Similar problems have been noted with the early transition metals.¹⁷

Hence, we employ a quasirelativistic pseudopotential approach that explicitly treats the penultimate shell on the metal (10-valence-electron effective core potentials, 10-ve-ECP); see Ref. 13 for similar pseudopotentials. This still saves considerable computation time and storage space as compared to high-level all-electron calculations (particular-
ly for the heavier metals) and avoids the problems of the 2-
ve-ECP approach. All-electron, 10-ve-ECP and 2-ve-ECP
calculations (the latter with and without a semiempirical
core-polarization potential) are compared for the mono-
hydridic systems where both accurate experimental data14
and a variety of theoretical studies11(b)-11(e) are available) and for the
monohydride cations (systems with approximately doubly
charged metals which have been examined theoretically-
ly15,16).

The dihydrides of Ca, Sr, and Ba are our major interest.
While neither experimental nor sufficient ab initio data are
available, the systems are small enough to allow a thorough
evaluation of the results using different pseudopotentials
and basis sets, as well as the effects of electron correlation.
For example, the basis set on F is very critical for the
difluorides.4(d) The dihydrides are easier to calculate accu-
rately.

In spite of its inherent problems, the 2-ve-ECP approach
together with the core-polarization potential sheds some light
on the relative importance of valence-shell d-orbital
participation vs core polarization as causes for the bent geo-
metries.

As we do not consider these systems to be fundamental-
different from other strongly ionic MX2 compounds of the
heavier group-II elements, many of the conclusions reached
for the hydrides should be transferable to a wider variety of
compounds.

II. METHODS

The 10-ve-valence electron pseudopotentials were adjusted
in a multielectron fit12 (MEFIT) to quasirelativistic17 ex-
itation and ionization energies for M0 and M+ using the
numerical atomic Hartree–Fock program MCHF77.18 Simi-
lar potentials using nonrelativistic HF energies also have been
obtained. The analytic form of the semilocal potentials is
given in Eqs. (1) and (2).12

\[
V(r) = - \frac{Q}{r} + \sum_{i=0}^{n} \sum_{\ell=1}^{l_{\text{max}}} C_{\ell} \exp(-c_{\ell}r^{2}) \cdot P_{\ell},
\]

\[
P_{\ell} = \sum_{m=-\ell}^{\ell} \left| Y_{\ell m} \right| \left( Y_{\ell m} \right)^{*}.
\]

Q is the core charge and P_{\ell} is the projector on angular momen-
tum l. The parameters of the pseudopotentials are listed in
the Appendix (cf. Table V).

Gaussian-type orbital (GTO) basis sets with six s and
four p functions have been optimized for the atomic ground
state. Two diffuse p functions to minimize the energy of the
lowest excited 3P state and five d functions to optimize the
lowest excited 3D state of the atom have been added to give
6s6p5d basis sets.

Single-electron-fit 2-valence-electron pseudopotentials
were taken from Fuentealba et al.11(b),15.19 Four s functions
optimized for the atomic ground state, four p functions opti-
mized for the lowest excited 3P state and the five d sets men-
tioned above together give the 4s4p5d-valence basis sets used
for these pseudopotentials. For comparison, in some cases
the five d sets have been replaced by the two d functions
(lacking larger exponents) used by Fuentealba et al.11(b),15
to give 4s4p2d basis sets. The optimized s and p basis sets
should be adequate even in view of the five d functions. We
have performed some test calculations on MH molecules by
employing the even tempered 7s5p basis sets of Fuentealba
et al.11(b),15 together with the five d functions and found
excellent agreement between the results for the 4s4p5d and
7s5p5d basis sets (with the same shortcomings; see below).

All unpublished basis-set exponents and contraction coeffi-
cients are listed in the Appendix (cf. Tables VI and VII).

For the simulation of the interaction between polariz-
izable M2+ cores with the valence electrons and H nuclei, a
semiempirical polarization potential (V_{\text{pol}}) as described in
Eqs. (3) and (4),19,20 and applied to Ca, Sr, and Ba before by
Fuentealba et al.11(b),15,19 has been used in conjunction with
the 2-ve-ECP approach:

\[
V_{\text{pol}} = - \alpha_{p}(f(g^{-1}r))^{2},
\]

\[
g(r) = \left( 1 - \exp(-\delta r^{2}) \right)^{1/2}.
\]

f is the field generated by valence electrons and surrounding
cores at the site of a given core, \alpha_{p} is the core dipole polari-
zability, and \delta is a cutoff parameter. This analytical form in-
cludes charge–dipole interactions but cannot provide di-
pole–dipole contributions. However, Guido and Gigli18 have
found that dipole–dipole interactions only play a minor role
for the XMX-bending effects we want to study in this work.

All-electron calculations involving Ca employed Wachters' basis set21(a)
which was completely decontracted and augmented by the two diffuse p functions optimized for
the 10-ve-ECP, one p function (\alpha = 0.1522)21(b) in order to
bridge the gap between 3p and 4p orbitals, and the five d functions optimized for the 10-ve-ECP to give a 14s12p5d
basis set. This basis gives an atomic energy for Ca of
- 676.7497 a.u. [HF limit of - 676.7582 a.u. (Ref. 18)].
For Sr the 16s10p4d basis set of Ref. 21(c) was augmented
by two diffuse p functions (with the same exponents as
for the 10-ve-ECP; see the Appendix). The most diffuse d func-
tions were replaced by the optimized 5-d set (see the Appen-
dix) to give a 16s12p8d basis set [E_{Sr} = 3129.1322 a.u.,
HF limit of 3131.5457 (Ref. 18)]. For Ba the 19s13p7d basis
set of Ref. 21(c) was augmented by two diffuse p functions
(see the Appendix) and four d functions (smaller exponents
of optimized 5-d set) to give a 19s15p11d basis set
[E_{Ba} = - 7878.9663 a.u., HF limit of - 7883.5438 (Ref.
18)]. Both for pseudopotential and all-electron calculations
the 5s2p basis set of Botschwina and Meyer21(d) for hydro-
gen was employed. As has been shown earlier for MH,11(c)
additional diffuse s and p functions are not necessary.

Valence- and core-valence correlation (the latter for the
10-ve-ECP and all-electron calculations) were included via a
singles–doubles configuration-interaction (CI) with Davi-
sdon's correction22 (SDCI + Q). For some of the SDCI + Q
calculations using the 10-ve-ECP approach, the influence of
adding one set of f functions (\alpha = 1.43, 0.97, 0.65 for
M = Ca, Sr, Ba, respectively), CI-optimized for MH, was
studied.

Molecular all-electron self-consistent-field (SCF) cal-
culations for M = Sr, Ba were carried out with the CASSCF
code23 (this program employs six Cartesian d functions) on
a Cray–YMP in Munich, pseudopotential SCF calculations
with GAUSSIAN 88 (Ref. 24) on the convex C210 in Erlan-
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III. RESULTS AND DISCUSSION

A. MH and MH⁺

The MH distances for MH and MH⁺, calculated with various methods, are summarized in Table I. Generally, SCF values clearly overestimate the experimental distances for MH, while the agreement between all-electron and 10-ve-ECP values is excellent for M = Ca and Sr and still reasonable for Ba.

The small deviations for M = Ba are due to relativistic effects. Test SCF calculations using the nonrelativistic 10-ve-ECP for Ba yield distance of 2.307 and 2.183 Å for BaH and BaH⁺, respectively, in perfect agreement with the all-electron SCF calculations. A very small influence of relativistic effects for BaH⁺ had been noted earlier by Pyykkö¹⁶ and was attributed to the involvement of s, p, and d orbitals in bonding. The relativistic contraction of the s and p orbitals is compensated (or slightly overcompensated) by the expansion of the d orbitals. This was taken as an indication for significant d orbital participation.

Explicit inclusion of core-valence correlation decreases the difference to the experiment. F functions obviously are important for angular correlation. These effects have been found before for CaH⁻¹¹(4d),¹¹(5d) The discrepancy to the experimental values is increasing from Ca to Ba. For MH⁺ the effects are similar to those found for MH but slightly smaller.

The values obtained at the SCF level with the 2-ve-ECP should be larger than those for the 10-ve-ECP and all-electron calculations as the static core polarization (both MH and MH⁺ have a permanent dipole moment) cannot be obtained from the frozen-core calculations. This is only true if the 4s4p2d basis sets are employed; the results are virtually identical to those obtained by Fuentealba et al.¹¹(b),¹⁵ with 7s5p2d basis sets using the same diffuse 2-d set. When the d functions are replaced by the 5-d set optimized for the 10-ve-ECP, which includes quite large d exponents (see the Appendix), the agreement between 2-ve-ECp, and 10-ve-ECP values is quite good. If core polarization is included by use of a polarization potential, the 4s4p2d basis-set results are extremely close to the experimental MH values. Results with this basis set also are very similar to those by Fuentealba et al.¹¹(b),¹⁵ (some deviations for MH⁺ may reflect the use of a density-functional approach by these authors to account for valence correlation¹⁵). However, for M = Ba there is no agreement when the 4s4p5d basis set is employed. This indicates problems with the 2-ve-ECP approach particularly for the heavy Ba. The projector for l = 2 of the pseudopotential could be identified as the source of this problem (this parallels earlier observations on CaO [Ref. 11(a)]). The d projector for the 2-ve-ECP has to simulate the attractive exchange contributions between valence-space (n − 1)-d and core (n−1)-s and p orbitals. This is not the case for the 10-ve-ECP. Since all these orbitals occupy a very similar region in space, the d projector of the 2-ve-ECP suffers a breakdown when inclusion of compact d functions in the basis set allows a considerable population of the (n−1)-d orbitals in the molecular systems. This cannot be avoided by addition of repulsive terms to the original attractive one.

Despite the apparent agreement between polarized-core 2-ve-ECP data employing the 4s4p2d basis sets and experiment, the 2-ve-ECP approach is certainly unsatisfactory from a theoretical point of view. An improvement in the basis set eliminates a fundamental axiom of the method, namely the assumed separation of core and valence shell. However, even the calculations using the 4s4p5d basis sets still produce quite reasonable results for M = Ca, Sr, and the magnitude of the error for M = Ba is not significantly larger than the error for the 10-ve-ECP SDCI calculations without f functions. Perhaps the polarized-core 2-ve-ECP approach should not be discarded altogether.

B. MH₂

1. Comparison of the different levels of theory

Let us now turn to the species of central interest in this work, the dihydrides. Table II presents the MH distances, the bending angles, as well as the energy changes and bond contractions upon bending obtained with various methods. CaH₂ is generally found to be linear [in agreement with Ref. 4(f)], so only the CaH distances are given. As for MH and MH⁺, the agreement between all-electron and 10-ve-ECP calculations is good for M = Ba and almost perfect for M = Ca and Sr. Nonrelativistic 10-ve-ECP SCF calculations for BaH₂ give a BaH distance of 2.361 Å and an angle of 121.6°. Apparently the relativistic effects are even smaller than for BaH and BaH⁺. The effect of core-valence correlation (and f functions) on the MH distances is of the same order of magnitude as for MH and MH⁺. This leads us to estimate the MH distances for these yet experimentally unknown molecules to be approximately 2.03 (2), 2.18 (2), and...
TABLE II. MH distances (Å), HMH bending angles (deg), bending energies ΔE_b (kcal/mol), and bond contraction AR* (Å) upon bending for the MH2 molecules (M = Ca, Sr, Ba) with different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>CaH2</th>
<th>SrH2</th>
<th>BaH2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M-H</td>
<td>M-H</td>
<td>IMHII</td>
</tr>
<tr>
<td>All-el. b</td>
<td>2.085</td>
<td>2.237</td>
<td>141.8</td>
</tr>
<tr>
<td>SCF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDCI + Q</td>
<td>2.063</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-ve-ECPc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF</td>
<td>2.081</td>
<td>2.231</td>
<td>142.5</td>
</tr>
<tr>
<td>SDCI + Q</td>
<td>2.062</td>
<td>2.211</td>
<td>141.2</td>
</tr>
<tr>
<td>SDCI + Q/2d</td>
<td>2.055</td>
<td>2.201</td>
<td>139.6</td>
</tr>
<tr>
<td>2ve-ECPa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V_2v/5d</td>
<td>2.006</td>
<td>2.222</td>
<td>180.0</td>
</tr>
<tr>
<td>V_2v/2d</td>
<td>2.063</td>
<td>2.223</td>
<td>144.3</td>
</tr>
<tr>
<td>V_2v/1d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF/5d</td>
<td>2.063</td>
<td>2.222</td>
<td>180.0</td>
</tr>
<tr>
<td>SDCI + Q/5d</td>
<td>2.065</td>
<td>2.223</td>
<td>180.0</td>
</tr>
</tbody>
</table>

*CaH2 is linear at all levels of approximation.
*bAll-electron calculations.
*c10-valence-electron pseudopotentials.
*dF functions added.
*e2-valence-electron pseudopotentials.
*fSDCI + Q calculations with core-polarization potential.
*gOnly 2 d functions used [cf. Refs. 11 (b) and 15].
*hD functions completely omitted.

2.2/\(3\) Å for CaH2, SrH2, and BaH2, respectively.

The bending angles, energy changes, and bond contracts upon bending are only moderately dependent on core-valence correlation and the presence of \(f\) functions in the SDCI calculations. This indicates that for SrH2 and BaH2, the major effects leading to bent geometries to a large extent are treated adequately at the HF level (the small effect of correlation on the bending angle for almost saturated basis sets has been noted by other authors for CaF2 [Ref. 4(d) and 4(e)].

The frozen-core 2-ve-ECP calculations obviously cannot reproduce the bent geometries for SrH2 and BaH2 (cf. Table II) even when the large \(d\) basis is employed. Bending is observed only upon inclusion of the core-polarization potential. This indicates, that, indeed, core polarization must be important. It is difficult to judge whether the values for SrH2 and BaH2 are reasonable, but in view of the 10-ve-ECP SDCI calculations it appears as if the distances might be underestimated. For SrH2, the angle also appears to be somewhat too small. This may be connected to the problems with the 2-ve-ECP approach discussed above. As core-valence correlation in the 10-ve-ECP SDCI calculations certainly is not treated completely, these values and those of the polarized-core 2-ve-ECP calculations with the 4s4p5d basis sets may be regarded as upper and lower bounds to the correct values. When the 4s4p2d basis set is used for the polarized-core 2-ve-ECP calculations, SrH2 is found to be linear, and the bending tendency for BaH2 decreases. When the \(d\) functions are removed completely, BaH2 also becomes linear.

For calculations on larger molecules, contracted basis sets are desirable to reduce the amount of computational effort. Therefore we have studied the effect of contracting either the \(d\) functions or the inner \(s\) and \(p\) functions of the 6s6p5d basis sets for 10-ve-ECP calculations on the geometries of SrH2 and BaH2 (cf. Table III). Apparently the contraction of the five \(d\) functions into two sets with three and two primitives, respectively, does not alter the geometry of BaH2 significantly, while the HMH angle for SrH2 increases by \(\sim 2^\circ\). Contraction into one group, however, gives a linear geometry for SrH2 and also introduces errors (notably for

<table>
<thead>
<tr>
<th>Contraction pattern</th>
<th>SrH2</th>
<th>BaH2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH</td>
<td>HMH</td>
<td>E_\text{val}</td>
</tr>
<tr>
<td>111111/111111/111111</td>
<td>2.23</td>
<td>142.5</td>
</tr>
<tr>
<td>111111/111111/32</td>
<td>2.234</td>
<td>144.3</td>
</tr>
<tr>
<td>111111/111111/5</td>
<td>2.270</td>
<td>180.0</td>
</tr>
<tr>
<td>21111/21111/32</td>
<td>2.234</td>
<td>144.4</td>
</tr>
<tr>
<td>3111/3111/52</td>
<td>2.225</td>
<td>146.5</td>
</tr>
</tbody>
</table>
the MH distance) for BaH$_2$. Obviously, at least the flexibility of two d groups is needed to obtain reasonable results.

Rows 4 and 5 in Table III evaluate the effect of contracting the inner s and p functions that are predominantly used to describe the $(n-1)$-s and -p orbitals. For BaH$_2$, apparently the contraction of the three inner s and p functions, respectively, into one group seems to be without consequence for the geometry even though the valence energy is affected more than after contraction of five d functions into one group. For SrH$_2$, with its more shallow bending potential, however, the HSrH angle is increased by about 4° upon contraction into 3111/33, whereas the contraction of only the two largest s and p exponents appears to leave the basis set flexible enough.

These results indicate that for larger molecules careful contraction of the basis sets may still produce reasonable results with reduced computational effort. For molecules where a relatively steep potential curve for the bending motion is expected (e.g., for BaH$_2$), a 3111/33 contraction pattern still seems to yield good geometries (apart from the error in the distances due to the neglected core-valence correlation). For systems with a relatively flat bending potential (as for SrH$_2$), a 2111/2111/32 contraction is recommended. For systems with extremely flat bending potentials (as, e.g., CaF$_2$ (Ref.4)), however, accurate bending angles will be very hard to obtain even with the uncontracted basis sets or still larger ones.

2. Discussion of the bent structures

All factors that favor bent geometries (i.e., core polarization, d-orbital participation) increase from Ca to Ba, whereas the major effect that opposes bending—repulsion of the hydride anions—decreases due to the larger distances. Hence, the increased tendency for BaH$_2$ to bend is not surprising.

The force constants calculated with the 10-ve-ECP at the SCF level (see Table IV) confirm that the potential curve for the bending motion in CaH$_2$ is extremely flat. This is similar to the situation found for CaF$_2$ (Ref.4). For a large range of HCaH angles the effects that favor or oppose bending almost cancel each other. The bending force constants increase considerably from SrH$_2$ through BaH$_2$ while the force constants for the MH stretch are decreasing. For SrH$_2$, the bending force constants and the relatively small energy gain upon bending (see Table II) still indicate a very floppy molecule. In contrast BaH$_2$ is genuinely bent. This is also true for many other BaX$_2$ systems where X is a strongly electronegative group. For the relatively steep bending potential well in BaH$_2$, small energy differences from errors in the calculations (e.g., neglect of zero-point vibration or incomplete treatment of electron correlation) will not lead to large changes in the bending angle. Therefore, we consider the calculated MBaH angle to be accurate within ±5°. This is significant because the existence of "abnormal" shapes for high-temperature AB$_x$ molecules has been doubted even quite recently.

Recently, v. Szentpály and Schwerdtfeger argued that the alkaline-earth core polarizabilities are too small to compensate for the loss in Coulombic energy upon bending. In their view core polarization does not fully explain the bent geometries. The data in Table II support this conclusion. If the d functions only served as "virtual orbitals of the core," i.e., to polarize the $(n-1)$-s and -p shell, there should be no large dependence of the bending angle on the d basis when the polarized-core 2-ve-ECP is employed. On the other hand, the 2-ve-ECP data without core-polarization potential fail to reproduce the bent geometries. This indicates that a pure sd-hybridization model that considers only the valence shell, a "frozen-core model," also is not adequate to explain the bent geometries. Therefore, a relatively simple model for the bent structures of ionic MX$_2$ systems only seems to work if both aspects are operative. The model proposed by v. Szentpály and Schwerdtfeger based on differences in atomic—or fragment—softness between metal center and substituents seems to meet this criterion (it predicts SrH$_2$ and BaH$_2$ to be bent, while CaH$_2$ would be a borderline case). This might be a good model as softness is related both to polarizability and via the highest occupied molecular-orbital—lowest unoccupied molecular-orbital (HOMOLUMO) gap also to covalent d-orbital participation.

We feel that more ab initio data on a large variety of compounds are necessary to evaluate the merits and shortcomings of the model. The 10-ve-ECP approach presented here should serve well for this purpose. This approach seems to be the method of choice for ab initio calculations on compounds of Ca, Sr, and Ba (and probably for Ra, which we also consider interesting in the future). The 10-ve-ECP calculations combine the accuracy of the best all-electron calculations, which for Sr and Ba are barely feasible even for the small dihydride molecules, with considerably less computational effort. Additionally, this pseudopotential approach treats the heavier alkaline-earth elements on equal footing as 10-valence-electron systems and includes the major relativistic effects.

<table>
<thead>
<tr>
<th>Mode</th>
<th>CaH$_2$</th>
<th>SrH$_2$</th>
<th>BaH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega$</td>
<td>$k$</td>
<td>$\omega$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>157</td>
<td>0.0153</td>
<td>213</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>1336</td>
<td>1.0605</td>
<td>1237</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1257</td>
<td>0.9843</td>
<td>1148</td>
</tr>
</tbody>
</table>


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The present results for the MH₂ molecules—the smallest MX₂ systems possible for Ca, Sr, and Ba—emphasize the generality of the bending effects. The theoretical study of small molecules may help to improve the understanding of the chemical aspects of the heavy alkaline-earth elements.

ACKNOWLEDGMENTS

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M.K. acknowledges a Kékulé grant by the Fonds der Chemischen Industrie. Thanks are also due to Professor H. J. Werner (Bielefeld) for providing his Cray-2 version of the program MOLPRO.

APPENDIX: PSEUDOPOTENTIAL AND BASIS-SET PARAMETERS

Tables V–VII contain all pseudopotential and basis-set parameters used in this work that have not been published previously.

TABLE V. Parameters of 10-valence-electron pseudopotentials for M = Ca, Sr, and Ba.

<table>
<thead>
<tr>
<th>M</th>
<th>l</th>
<th>Exponent</th>
<th>Coefficient</th>
<th>QR* Exponent</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0</td>
<td>11.227 562 1</td>
<td>138.845 701 8</td>
<td>11.231 672 5</td>
<td>138.785 174 6</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.649 919 26</td>
<td>17.024 774 12</td>
<td>4.761 960 02</td>
<td>16.504 244 08</td>
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<td>11.156 907 3</td>
<td>83.123 664 45</td>
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<td>4.816 964 88</td>
<td>13.771 547 38</td>
<td>4.810 141 10</td>
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<td>13.775 936 2</td>
<td>-16.206 485 7</td>
<td>13.754 728 4</td>
<td>-16.201 965 2</td>
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<td>4.787 728 97</td>
<td>-1.64 480 88</td>
<td>4.762 469 79</td>
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<td>Ba</td>
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<td>12.765 845 6</td>
<td>-26.728 178 1</td>
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<td>1</td>
<td>7.400 074 34</td>
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<td>3.606 379 11</td>
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<td>1.170 952 0</td>
<td>29.888 986 84</td>
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*Quasirelativistic pseudopotentials.

TABLE VI. 6s6p5d basis sets for the 10-valence-electron pseudopotentials.

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<tr>
<th>M</th>
<th>s exp.</th>
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<th>p exp.</th>
<th>p coeff.</th>
<th>d exp.</th>
<th>d coeff.</th>
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<tr>
<td>Ca</td>
<td>12.307 521</td>
<td>0.058 740</td>
<td>5.974 286</td>
<td>-0.082 302</td>
<td>7.231 700</td>
<td>0.050 360</td>
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<td></td>
<td>4.393 131</td>
<td>-0.401 344</td>
<td>1.367 406</td>
<td>0.346 511</td>
<td>1.964 869</td>
<td>0.173 343</td>
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<td>0.937 975</td>
<td>0.592 875</td>
<td>0.656 242</td>
<td>0.560 147</td>
<td>0.620 103</td>
<td>0.301 978</td>
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<tr>
<td></td>
<td>0.421 688</td>
<td>1.0</td>
<td>0.258 498</td>
<td>1.0</td>
<td>0.181 260</td>
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<td>0.028 017</td>
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<td>0.031 834</td>
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<td>0.099 101</td>
<td>0.464 720</td>
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<td>Sr</td>
<td>5.870 157</td>
<td>0.196 709</td>
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<td>-0.374 899</td>
<td>3.618 081</td>
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<td>3.092 482</td>
<td>-0.625 898</td>
<td>1.664 234</td>
<td>0.387 615</td>
<td>0.996 656</td>
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<td>0.644 667</td>
<td>0.735 723</td>
<td>0.569 985</td>
<td>0.655 838</td>
<td>0.390 735</td>
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<td>0.220 718</td>
<td>1.0</td>
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<td>0.477 318</td>
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<td>1.0</td>
<td>0.067 629</td>
<td>1.0</td>
<td>0.036 655</td>
<td>0.448 183</td>
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<td>-5.328 895</td>
<td>2.926 742</td>
<td>0.763 359</td>
<td>0.966 315</td>
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<td>2.243 305</td>
<td>6.646 934</td>
<td>2.520 718</td>
<td>-1.022 014</td>
<td>0.893 828</td>
<td>0.947 240</td>
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<tr>
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<td>0.717 402</td>
<td>-0.351 437</td>
<td>0.524 095</td>
<td>0.649 836</td>
<td>0.273 195</td>
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<td>0.278 446</td>
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<td>0.203 428</td>
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<td>0.103 891</td>
<td>0.473 260</td>
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<td>0.043 188</td>
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<td>1.0</td>
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<td>0.019 798</td>
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TABLE VII. 4s4p-valence basis sets for the 2-valence-electron pseudopotentials.

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<th>( r_{\text{exp}} )</th>
<th>( r_{\text{cof}} )</th>
<th>( \rho_{\text{exp}} )</th>
<th>( \rho_{\text{cof}} )</th>
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<tbody>
<tr>
<td>Ca</td>
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<td>0.106 831</td>
<td>0.316 915</td>
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<td>0.432 313</td>
<td>-0.207 240</td>
<td>0.116 016</td>
<td>0.238 641</td>
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<tr>
<td>Sr</td>
<td>0.791 740</td>
<td>0.083 514</td>
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<tr>
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<td>0.316 178</td>
<td>-0.429 237</td>
<td>0.095 691</td>
<td>0.255 497</td>
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<tr>
<td>Ba</td>
<td>0.492 847</td>
<td>0.228 967</td>
<td>0.153 752</td>
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<td>0.020 856</td>
<td>0.518 935</td>
<td>0.014 238</td>
<td>0.231 287</td>
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</table>

\* Cf. Ref. 29.