

Pseudopotential approaches to Ca, Sr, and Ba hydrides. Why are some alkaline earth MX_2 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 MH_2 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 SrH_2 and BaH_2 to be bent with angles of $\sim 140^\circ$ and 120° , respectively, while CaH_2 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 SrH_2 and BaH_2 . 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 MX_2 compounds of the heavier alkaline earth metals are still considered to be unsolved problems.¹

In 1963–1964 the electric-quadrupole deflection experiments of Klempner 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 model predictions [e.g., the valence shell electron pair repulsion (VSEPR) model,⁵ Walsh diagrams,⁶ or simple ionic, MO, and valence-bond pictures].

Recently, gas-phase electron-diffraction studies of MCp_2^* molecules ($\text{Cp}^* = \text{Me}_5\text{Cp}$) indicated that these phenomena would be of general importance in the emerging field of Ca-, Sr-, and Ba-organometallic chemistry.⁷

Two 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.⁸ The alternative model emphasizes the polarization of the large M^{+2} cations by the anions as being the main driving force for the bending.⁹ While the present work was in progress, v. Szentpály and Schwerdtfeger^{4d} 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 softness¹⁰ 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.^{4d}

Ab initio quantum-chemical calculations that might shed light on the problem usually focused on CaF_2 ,⁴ 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 previously^{4(d)-(f)} do not establish whether the equilibrium geometry of CaF_2 is bent or linear. Therefore, CaF_2 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.^{11(a),11(b)} 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.^{11(c)-11(e)} A clearcut separation between valence space and these orbitals is difficult to achieve. Similar problems have been noted with the early transition metals.^{12,13(a)}

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 monohydrides (where both accurate experimental data¹⁴ and a variety of theoretical studies^{11(b)-11(e)} are available) and for the monohydride cations (systems with approximately doubly charged metals which have been examined theoretically^{15,16}).

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 accurately.

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 geometries.

As we do not consider these systems to be fundamentally 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-valence electron pseudopotentials were adjusted in a multielectron fit¹² (MEFIT) to quasirelativistic¹⁷ excitation and ionization energies for M⁰ and M⁺ using the numerical atomic Hartree-Fock program MCHF77.¹⁸ Similar potentials using nonrelativistic HF energies also have been obtained. The analytic form of the semilocal potentials is given in Eqs. (1) and (2).¹²

$$V(r) = -\frac{Q}{r} + \sum_{l=0}^{l_{\max}} \sum_{i=1}^n C_{li} \exp(-c_{li}r^2) \cdot \mathbf{P}_l, \quad (1)$$

$$\mathbf{P}_l = \sum_{m_l=-l}^l |Y_{l,m_l}\rangle \langle Y_{l,m_l}|. \quad (2)$$

Q is the core charge and \mathbf{P}_l is the projector on angular momentum 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 ³*P* state and five *d* functions to optimize the lowest excited ³*D* state of the atom have been added to give 6s6p5*d* 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 optimized for the lowest excited ³*P* state, and the five *d* sets mentioned above together give the 4s4p5*d*-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 4s4p2*d* 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 7s5*p* basis sets of Fuentealba *et al.*^{11(b),15} together with the five *d* functions and found excellent agreement between the results for the 4s4p5*d* and 7s5p5*d* basis sets (with the same shortcomings; see below). All unpublished basis-set exponents and contraction coefficients are listed in the Appendix (cf. Tables VI and VII).

For the simulation of the interaction between polarizable M²⁺ cores with the valence electrons and H nuclei, a semiempirical polarization potential (V_{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:

$$V_{\text{pol}} = -\frac{1}{2}\alpha_D(\mathbf{f}(g^{-1}\mathbf{r}))^2, \quad (3)$$

$$g(r) = [1 - \exp(-\delta r^2)]^{1/2}. \quad (4)$$

\mathbf{f} is the field generated by valence electrons and surrounding cores at the site of a given core, α_D is the core dipole polarizability, and δ is a cutoff parameter. This analytical form includes charge-dipole interactions but cannot provide dipole-dipole contributions. However, Guido and Gigli⁹ 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 set^{21(a)} This 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 3*p* and 4*p* orbitals, and the five *d* functions optimized for the 10-*ve*-ECP to give a 14s12p5*d* 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 16s10p4*d* 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* function was replaced by the optimized 5-*d* set (see the Appendix) to give a 16s12p8*d* basis set [$E_{\text{Sr}} = 3129.1329$ a.u., HF limit of -3131.5457 (Ref. 18)]. For Ba the 19s13p7*d* 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 19s15p11*d* basis set ($E_{\text{Ba}} = -7878.9663$ a.u., HF limit of -7883.5438 (Ref. 18)]. Both for pseudopotential and all-electron calculations the 5s2*p* basis set of Botschwina and Meyer^{21(d)} for hydrogen was employed. As has been shown earlier for MH,^{11(b)} 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 Davidson'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) calculations for M = Sr, Ba were carried out with the CADPAC 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-

gen, SDCI calculations including a polarization potential with MELD (Ref. 25) (Cartesian d functions used), and all other SDCI calculations with MOLPRO (Ref. 26) on the Cray-2 in Stuttgart.

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 distances 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(d),11(e)} 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

TABLE I. Bond distances (Å) for MH and MH⁺ (M = Ca, Sr, Ba) with different methods.

Method	CaH	SrH	BaH	CaH ⁺	SrH ⁺	BaH ⁺
All-el. ^a						
SCF	2.050	2.194	2.304	1.930	2.065	2.178
SDCI + Q	2.029			1.915		
10- <i>ve</i> -ECP ^b						
SCF	2.047	2.196	2.329	1.926	2.068	2.196
SDCI + Q	2.031	2.181	2.309	1.918	2.063	2.193
SDCI + Q/ f^c	2.019	2.164	2.275	1.903	2.045	2.164
2- <i>ve</i> -ECP ^d						
$V_{\text{pol}}/5d^e$	1.997	2.140	2.156	1.868	1.979	2.064
$V_{\text{pol}}/2d^{ef}$	2.011	2.154	2.244	1.920	2.057	2.146
SCF/ $5d$	2.053	2.195	2.326	1.951	2.076	2.203
SCF/ $2d^f$	2.074	2.228	2.376	1.961	2.082	2.203
Expt. ^g	2.000	2.143	2.233			

^a All-electron calculations

^b 10-valence-electron pseudopotentials with $6s6p5d$ basis sets.

^c F functions added.

^d 2-valence-electron pseudopotentials.

^e SDCI + Q calculations with core-polarization potential

^f Only two d functions used [cf. Refs. 11(b) and 15].

^g Cf. Ref. 14.

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 (\AA), HMH bending angles (deg), bending energies ΔE_b (kcal/mol), and bond contraction ΔR_b (\AA) upon bending for the MH_2 molecules ($M = \text{Ca, Sr, Ba}$) with different methods.

Method	CaH_2^a		SrH_2			BaH_2			
	M-H	M-II	HMH	ΔE_b	ΔR_b	M-H	HMH	ΔE_b	ΔR_b
All-el. ^b									
SCF	2.085	2.237	141.8	0.59	0.028	2.356	121.3	5.65	0.109
SDCI + Q	2.063								
10 ve -ECP ^c									
SCF	2.081	2.231	142.5	0.60	0.030	2.366	121.9	4.91	0.098
SDCI + Q	2.062	2.211	141.2	0.89	0.021	2.342	119.4	5.54	0.100
SDCI + Q/ f^d	2.055	2.201	139.6	0.97	0.029	2.314	118.7	6.06	0.108
2 ve -ECP ^e									
$V_{\text{pol}}/5d^f$	2.000	2.127	133.5	0.88	0.041	2.199	117.9	8.43	0.140
$V_{\text{pol}}/2d^{f,g}$		2.196	180.0	0.00	0.000	2.266	120.6	3.84	0.095
$V_{\text{pol}}/0d^{f,h}$						2.355	180.0	0.00	0.000
SCF/ $5d$	2.063	2.222	180.0	0.00	0.000	2.391	165.3	0.01	0.007
SDCI + Q/ $5d$	2.065	2.220	180.0	0.00	0.000	2.387	164.4	0.03	0.006

^a CaH_2 is linear at all levels of approximation.

^b All-electron calculations.

^c 10-valence-electron pseudopotentials.

^d f functions added.

^e 2-valence-electron pseudopotentials.

^f SDCI + Q calculations with core-polarization potential.

^g Only 2 d functions used [cf. Refs. 11(b) and 15].

^h D functions completely omitted.

2.27(3) \AA for CaH_2 , SrH_2 , and BaH_2 , respectively.

The bending angles, energy changes, and bond contractions upon bending are only moderately dependent on core-valence correlation and the presence of f functions in the SDCI calculations. This indicates that for SrH_2 and BaH_2 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 CaF_2 [Refs. 4(d) and 4(e)]).

The frozen-core 2- ve -ECP calculations obviously cannot reproduce the bent geometries for SrH_2 and BaH_2 (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 SrH_2 and BaH_2 are reasonable, but in view of the 10- ve -ECP SDCI calculations it appears as if the distances might be underestimated. For SrH_2 , 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, SrH_2 is found to be linear, and the bending tendency for BaH_2 decreases. When the d functions are removed completely, BaH_2 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 SrH_2 and BaH_2 (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 BaH_2 significantly, while the HMH angle for SrH_2 increases by $\sim 2^\circ$. Contraction into one group, however, gives a linear geometry for SrH_2 and also introduces errors (notably for

TABLE III. The influence of basis-set contraction on the MH distances (\AA), HMH angles (deg), and valence energy (a.u.) of SrH_2 and BaH_2 (10- ve -ECP approach).

Contraction pattern	SrH_2			BaH_2		
	MH	HMH	E_{val}	MH	HMH	E_{val}
111111/111111/11111	2.231	142.5	-31.450 23	2.366	121.9	-26.188 73
111111/111111/32	2.234	144.3	-31.449 58	2.367	122.3	-26.188 35
111111/111111/5	2.270	180.0	-31.448 23	2.400	124.0	-26.183 61
21111/21111/32	2.234	144.4	-31.449 54	2.368	122.7	-26.187 95
3111/3111/32	2.235	146.5	-31.448 30	2.357	122.8	-26.172 22

the MH distance) for BaH₂. 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 BaH₂ 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 SrH₂ with its more shallow bending potential, however, the HSrH angle is increased by about 4° upon contraction into 3111/3111/32, 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 BaH₂), a 3111/3111/32 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 SrH₂) a 21111/21111/32 contraction is recommended. For systems with extremely flat bending potentials [as, e.g., CaF₂ (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 BaH₂ 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 CaH₂ is extremely flat.^{4(f)} This is similar to the situation found for CaF₂.⁴ 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 SrH₂ through BaH₂ while the force constants for the MH stretch are decreasing. For SrH₂ the bending force constants and the relatively small energy gain upon bending (see Table II) still indicate a very floppy molecule. In contrast BaH₂ is genuinely bent. This is also true for many other BaX₂ systems where X is a strongly

electronegative group.²⁷ For the relatively steep bending potential well in BaH₂ 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_{*n*} molecules has been doubted even quite recently.²⁸

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.^{4(d)} The data in Table II support this conclusion. If the *d* functions only served as “virtual orbitals of the core,”^{11(e)} 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 MX₂ systems only seems to work if both aspects are operative. The model proposed by v. Szentpály and Schwerdtfeger^{4(d)} based on differences in atomic—or fragment—softness between metal center and substituents seems to meet this criterion (it predicts SrH₂ and BaH₂ to be bent, while CaH₂ would be a borderline case). This might be a good model as softness¹⁰ is related both to polarizability and via the highest occupied molecular-orbital—lowest unoccupied molecular-orbital (HOMO-LUMO) 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 IV. Harmonic force constants *k* (mdyn/Å) and frequencies ω (cm⁻¹) for MH₂ (M = Ca, Sr, Ba) calculated at the 10-*ve*-ECP/6s6p5d-basis-set level.

Mode	CaH ₂		SrH ₂		BaH ₂	
	ω	<i>k</i>	ω	<i>k</i>	ω	<i>k</i>
δ	157	0.0153	213	0.0276	347	0.0724
ν_s	1336	1.0605	1237	1.0111	1147	0.7842
ν_{as}	1257	0.9843	1148	0.7982	1075	0.6933

The present results for the MH_2 molecules—the smallest MX_2 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 chemistry of the heavy alkaline-earth elements.

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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 $M = Ca, Sr, \text{ and } Ba$.

l	HF		QR ^a		
	Exponent	Coefficient	Exponent	Coefficient	
Ca	0	11.227 562 1	138.845 701 8	11.231 672 5	138.785 174 3
		4.649 919 26	17.024 774 12	4.671 960 02	16.504 244 08
	1	11.170 952 0	83.157 318 31	11.156 907 3	83.123 664 45
		4.816 964 88	13.771 547 38	4.810 141 10	13.502 271 90
	2	13.775 936 2	−16.206 485 7	13.754 728 4	−16.201 965 2
		4.787 728 97	−1.164 480 88	4.762 469 79	−1.132 389 8
3	12.765 845 6	−26.728 178 1	12.765 845 6	−26.728 178 1	
Sr	0	7.400 074 34	135.889 657 26	7.400 074 34	135.479 430 01
		3.606 379 11	20.623 319 50	3.606 379 11	17.534 463 16
	1	6.484 868 17	88.527 584 91	6.484 868 17	88.359 709 13
		3.288 052 69	16.652 996 34	3.288 052 69	15.394 371 59
	2	4.622 840 79	29.860 591 03	4.622 840 79	29.888 986 84
		2.246 903 88	6.495 101 33	2.246 903 88	6.659 413 99
3	4.633 975 34	−15.805 992 03	4.633 975 34	−15.805 992 03	
Ba	0	9.530 165 87	431.394 018 69	9.526 986 15	427.845 816 06
		4.409 395 71	265.471 849 02	4.487 509 93	204.417 530 09
	1	8.315 821 69	299.200 234 28	8.315 929 78	293.605 863 62
		4.328 506 73	354.250 266 99	4.292 217 18	294.193 315 95
	2	5.916 215 60	111.799 800 82	5.916 108 38	112.550 401 69
		2.889 258 04	177.015 930 01	2.874 842 20	181.782 620 81
3	3.589 464 68	−33.473 174 20	3.589 464 68	−33.473 174 20	

^a Quasirelativistic pseudopotentials.

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

	s exp.	s coeff.	p exp.	p coeff.	d exp.	d coeff.
Ca	12.307 521	0.058 740	5.974 286	−0.082 302	7.231 700	0.050 360
	4.393 151	−0.401 344	1.567 406	0.346 511	1.964 869	0.173 343
	0.937 975	0.592 875	0.656 242	0.560 147	0.620 303	0.301 978
	0.421 688	1.0	0.258 498	1.0	0.181 260	0.438 055
	0.058 017	1.0	0.083 252	1.0	0.049 107	0.464 720
	0.023 222	1.0	0.031 834	1.0		
Sr	5.879 157	0.196 709	2.432 472	−0.374 899	3.618 081	−0.007 501
	3.092 482	−0.625 898	1.664 234	0.387 615	0.996 656	0.108 098
	0.644 667	0.735 723	0.569 989	0.655 838	0.390 735	0.278 540
	0.298 876	1.0	0.220 718	1.0	0.122 770	0.477 318
	0.057 276	1.0	0.067 629	1.0	0.036 655	0.448 183
	0.023 870	1.0	0.026 727	1.0		
Ba	2.396 190	−5.328 895	2.926 742	0.763 359	0.966 315	−0.908 938
	2.243 305	6.646 934	2.520 718	−1.022 014	0.893 828	0.947 240
	0.717 402	−0.351 437	0.524 095	0.649 836	0.273 195	0.322 057
	0.278 446	1.0	0.203 428	1.0	0.103 891	0.473 260
	0.043 188	1.0	0.047 996	1.0	0.035 578	0.365 977
	0.019 798	1.0	0.020 095	1.0		

TABLE VII. 4s4p-valence basis sets for the 2-valence-electron pseudopotentials.^a

	<i>s</i> exp.	<i>s</i> coeff.	<i>p</i> exp.	<i>p</i> coeff.
Ca	0.838 265	0.106 831	0.316 915	-0.117 134
	0.432 313	-0.387 240	0.116 018	0.238 541
	0.065 110	0.645 409	0.049 708	0.598 632
	0.027 107	0.508 330	0.021 478	0.302 522
Sr	0.791 740	0.083 514	0.225 825	-0.167 335
	0.316 178	-0.429 237	0.095 691	0.255 497
	0.066 565	0.523 969	0.042 077	0.611 669
	0.026 990	0.673 733	0.018 077	0.301 854
Ba	0.492 847	0.228 967	0.153 752	-0.271 593
	0.282 844	-0.581 035	0.080 987	0.354 234
	0.044 874	0.667 308	0.032 566	0.664 264
	0.020 586	0.518 935	0.014 238	0.231 287

^a Cf. Ref. 29.

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