Theoret. Chim. Acta (Berl.) 50, 49–65 (1978)

THEORETICA CHIMICA ACTA

ab initio Calculations on Model Chains*

A. Karpfen

Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, Währingerstr. 17, A-1090 Wien, Austria

Ab initio calculations on the linear lithium chain, the linear lithium hydride chain and a beryllium hydride polymer have been performed using the crystal orbital method. The influence of an increase of the basis set, an increase in the number of neighbors and an increase of the density of k-points in the Brillouin zone on the calculated equilibrium geometries and band structures has been studied systematically. A proper description of the unit cell and the interaction between neighboring cells turned out to be most important. Energy bands were found to be extremely sensitive to any variation in the basis set applied.

Key words: Crystal orbital method – Lithium chain – Lithium hydride chain – $(BeH_2)_x$

1. Introduction

Nowadays, *ab initio* calculations on small and medium-size molecules at the Hartree–Fock level have almost become a matter of routine. On the other hand, for extended systems, like polymers, layers, and crystals, nonempirical calculations of near Hartree–Fock quality have not yet been performed. Although several methods have been developed to handle properly the problem of translational symmetry within the framework of the Hartree–Fock approximation [1–6], the accuracy of the Hartree–Fock method in extended systems has not yet been assessed quantitatively. Most actual applications have either been performed with rather limited basis sets or used rather drastic approximations with respect to the treatment of lattice sums. The crucial importance of the use of extended basis sets in the

---

* This work has been supported by the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung" (Project Nr. 2756).

quantum mechanical treatment of molecules has generally been accepted [7, 8]. Polymers or crystals can be viewed as "large" molecules, hence it is only to be expected that for a correct description of these systems the basis set problem plays a central role.

The aim of this work is to present extensive numerical investigations on the various convergence problems, which arise in a theoretical treatment of extended systems. Since *ab initio* studies on these systems are rather time-consuming, we restricted ourselves to one-dimensional model systems. To be able to discuss also physically different situations, we chose as representative examples the linear, metallic lithium chain, the ionic lithium hydride chain and a beryllium hydride polymer. The latter is largely covalent, but still has some ionic character. The case of a hydrogen-bonded chain has already been treated previously by us [9].

The criteria for choosing these model systems were, apart from the chemical point of view, mainly determined by economical reasons. Only systems with light atoms and small unit cells allow a systematic investigation of the influence of basis set, number of neighbors, and number of k-points on the computed ground state properties, as for example equilibrium geometries, force constants, stabilization energies per unit cell and the band structure of occupied bands. A concomitant drawback is therefore that the numerical results obtained in the present investigation can hardly be compared with experiment directly. They should rather be understood as a further step on the way to obtain a more accurate description of extended systems. Additionally they could possibly serve to get a better understanding of the technical problems which are involved in a Hartree–Fock treatment of periodic systems and give some useful hints for further applications.

2. Method of Calculation

Throughout this work the Crystal-Orbital (CO) formalism was used which has been developed simultaneously and independently by two different groups [1, 2]. The advantage of this approach lies in the fact that it is a straightforward extension of the usual Hartree–Fock procedure to periodic systems and hence monomers, dimers, small clusters and extended systems can be studied conveniently at the same level of approximation. Although a large number of *ab initio* calculations using the CO method has recently been published [10–15], only certain aspects of the various convergence problems connected with this technique have been treated. The influence of the number of neighbors taken into account has been studied for the case of a linear hydrogen chain in one particular geometrical arrangement, using a fixed (STO-4G) basis set [43]. The influence of an improvement in the basis set applied has been investigated for a bent hydrogen fluoride chain, again at a fixed geometry [44]. A systematic study of these methodical aspects including geometry optimization as well is still missing.

To facilitate a discussion of the methodical problems connected with CO calculations, we shortly recall the necessary equations (see Refs. [1] and [16]). The complex pseudoeigenvalue problem which has to be solved point by point in

k-space can be written as

$$F'(k)\,d(k)=\varepsilon(k)S'(k)\,d(k) \tag{1}$$

where

$$F'(k)=\sum_{q=-\infty}^{+\infty} e^{ikR_q}F(q) \tag{2}$$

and

$$S'(k)=\sum_{q=-\infty}^{+\infty} e^{ikR_q}\,S(q). \tag{3}$$

The elements of the matrices $F(q)$ and $S(q)$, respectively, are defined as

$$\begin{aligned}[F(q)]_{r,s}=\langle\chi_r^0|-\tfrac{1}{2}\Delta-\sum_{q=-\infty}^{+\infty}\sum_{\alpha=1}^{M}\frac{Z_\alpha}{|r-R_\alpha^q|}|\chi_s^q\rangle\\ +\sum_{q_1=-\infty}^{+\infty}\sum_{q_2=-\infty}^{+\infty}\sum_{u,v}P(q_1-q_2)_{u,v}(\langle\chi_r^0\chi_s^q|\chi_u^{q_1}\,\chi_v^{q_2}>-\mathrm{exch})\end{aligned} \tag{4}$$

$$[S(q)_{r,s}=\langle\chi_r^0|\chi_s^q\rangle. \tag{5}$$

The density matrices occurring in Eq. (4) are determined by a numerical integration over the first Brillouin zone:

$$P(q_1-q_2)_{u,v}=\frac{a}{2\pi}\int_{-\pi/a}^{+\pi/a}\sum_{h=1}^{\mathrm{occ}} d(k)_{h,u}^{*}\,d(k)_{h,v}\,e^{ika(q_1-q_2)}\,dk \tag{6}$$

where a is the length of the unit cell. The total energy per unit cell is hence defined as

$$E/\mathrm{cell}=\frac{a}{2\pi}\int_{-\pi/a}^{+\pi/a}\sum_{h=1}^{\mathrm{occ}}[I(k)_{h,h}+\varepsilon(k)_h]\,dk\quad+\text{nuclear repulsion} \tag{7}$$

where

$$I(k)_{h,h}=d(k)_h^{*}I(k)\,d(k)_h \tag{8}$$

and

$$I(k)=\sum_{q=-\infty}^{+\infty} e^{ikR_q}I(q) \tag{9}$$

where the $I(q)$'s are the one-electron parts of the Fock matrices $F(q)$.

Besides the usual convergence problems, which are known from the standard Hartree–Fock procedure for molecules, namely convergence with respect to the basis set used, and convergence within the SCF cycle, one has additionally to deal with the summations in Eqs. (2) and (3), which correspond to lattice sums. Finally convergence with respect to the number of k-points in the Brillouin zone which is used for the integrations in Eqs. (6) and (7) has to be achieved.

For all calculations presented in this work a SCF convergence criterion of $1.0 \cdot 10^{-6}$ for the density matrices was applied. Basis sets were taken from Refs. [17] and [18], and additional polarization functions have been optimized with respect to the total energy, to obtain more flexibility in the valence region. For two reasons this optimization was performed for the isolated molecules only. Firstly, a comparison between total energies of the monomers and total energies per unit cell for the infinite systems is easier if the same basis sets are used. This is quite justified if the basis set used has enough flexibility to describe properly both cases. Secondly, optimization in the periodic systems is somewhat problematic because of near-linear-dependence problems. Due to truncations of the lattice sums in Eqs. (2) and (3) the matrices $S(k)$ may either be non-positive definite or may have very small eigenvalues. The same difficulties are encountered if basis functions with too small exponents are used. The overlap matrices may also have already converged, but the resulting small eigenvalues cause numerical problems. Therefore, in the process of optimizing additional functions one often cannot find an energy minimum, but directly enters a region where unreasonable results are obtained. This problem has been recognized a long time ago [19], but has to be kept in mind for actual calculations. The numerical integrations in Eqs. (6) and (7) have been performed according to Simpson's rule.

For the case of the lithium chain and the lithium hydride chain seven points have been computed around the equilibrium geometry to determine the force constants. The equilibrium geometries of the beryllium hydride dimer, trimer and polymer have been determined by computing five points along each coordinate plus several coupling points. The resulting hypersurface was fitted by two- and three-dimensional polynomials of third degree.

3. The Linear, Metallic Lithium Chain

As a simple model for a metallic system a hypothetical, linear lithium crystal was selected. The metallic lithium crystal has been treated several times by *ab initio* techniques. The GI method has been applied by O'Keefe and Goddard [20, 21]. Calais and Sperber [22] used the AMO method, whereas Kumar, Monkhorst and Harris [23, 24] used a fourier transform technique. Stoll and Preuß described an approach which takes advantage of the different convergence behavior of the lattice sums in direct and reciprocal space [5]. The only *ab initio* calculation on a linear lithium chain performed so far used an STO 3G basis set [25].

Due to the smallness of the unit cell, which contains only one lithium atom, extensive investigations of the influence of basis set, number of neighbors and number of k-points could be performed. In addition to calculations on the metallic lithium chain, the case of a molecular chain built up from Li_2 molecules was considered as well. Both the intermolecular and the intramolecular distances were varied independently. Whereas pure s basis sets still give a minimum at an intermolecular distance of about 7.0 a.u., while the intramolecular distance is practically unchanged, this artifact, which can be traced back to the well known superposition error, vanishes, if polarization functions are added. Thus the lithium

Table 1. Total energy per unit cell and band structure of the infinite, metallic lithium chain at $r_{Li-Li} = 5.9$ a.u., with different number of neighbors and different *k*-points using a 6*s*-basis[a]. All values are given in a.u.

Number of neighbours	Number of *k*-points	Total energy per unit cell	$\varepsilon_{1s}(0)$	$\varepsilon_{1s}(\pi)$	Δ_{1s}^{b}	$\varepsilon_{2s}(0)$	$\varepsilon_{\mathrm{Fermi}}$	Δ_{2s}^{c}
1	21	−7.426584	−2.52676	−2.52700	0.00024	−0.23791	−0.20832	0.02959
2	21	−7.425010	−2.50750	−2.50722	0.00028	−0.26033	−0.11555	0.14478
3	21	−7.424656	−2.50051	−2.50035	0.00016	−0.23865	−0.12371	0.11494
4	21	−7.424660	−2.49679	−2.49672	0.00007	−0.22892	−0.11189	0.11703
6	21	−7.424715	−2.49292	−2.49281	0.00011	−0.23165	−0.10954	0.12211
8	21	−7.424747	−2.49089	−2.49080	0.00009	−0.22576	−0.10809	0.11767
10	21	−7.424766	−2.48966	−2.48955	0.00011	−0.22676	−0.10712	0.11964
6	13	−7.424736	−2.49292	−2.49281	0.00011	−0.23178	−0.10946	0.12232
6	17	−7.424719	−2.49292	−2.49281	0.00011	−0.23168	−0.10952	0.12216
6	25	−7.424714	−2.49292	−2.49281	0.00011	−0.23165	−0.10954	0.12211
6	33	−7.424713	−2.49292	−2.49281	0.00011	−0.23164	−0.10955	0.12209

[a] See Ref. [17].

[b] Bandwidth of the core band.

[c] Width of the occupied part of the valence band.

chain is unbound with respect to isolated Li_2 molecules at all distances in the Hartree–Fock approximation. This result could be expected for electrostatic reasons, since the quadrupole-quadrupole interaction is repulsive in the linear arrangement. Nevertheless for the case of an equidistant chain a local minimum exists, which means that the lithium chain is stable with respect to isolated lithium atoms.

For pilot calculations we used the 6*s* basis contracted to four groups. Table 1 shows the total energy per unit cell and the relevant data for the band structure of the infinite lithium chain at a fixed distance of 5.9 a.u., which is close to the equilibrium distance, as a function of the number of neighbors taken into account and the number of *k*-points used. In Table 2 the variation of the equilibrium

Table 2. Total energy per unit cell, equilibrium distance, force constant and valence band of an infinite, metallic lithium chain as a function of the number of neighbors and the number of *k*-points, using a 6*s* basis set[a]

Number of neighbours	Number of *k*-points	Total energy per unit cell [a.u.]	Equilibrium distance [a.u.]	Force constant [mdyne/Å]	$\varepsilon_{2s}(0)$ [a.u.]	$\varepsilon_{\mathrm{Fermi}}$ [a.u.]
4	13	−7.424670	5.8822	0.122	−0.22916	−0.11193
6	13	−7.424737	5.8918	0.121	−0.23199	−0.10951
6	33	−7.424713	5.8930	0.121	−0.23182	−0.10960
10	33	−7.424759	5.8966	0.121	−0.22678	−0.10716

[a] See Ref. [17].

distance, the force constant and the valence band structure for different number of neighbors and k points is given, using again the 6s basis.

An inspection of Tables 1 and 2 gives already an impression of the relative importance of these two convergence problems. Whereas the number of k-points has only a minor influence on the computed properties and calculations using the minimal number of k-points to avoid cyclic properties [26] give already quite reasonable results, convergence with respect to the number of neighbors turns out to be more important. It is especially noteworthy that reasonable results can only be obtained if at least three or four neighbors are included. Although the convergence pattern of the band structure is somewhat irregular one has to keep in mind that the physical meaning of the energy bands has to be interpreted via Koopmans' theorem [27]. Since the errors connected with the use of Koopmans' theorem in the interpretation of photoelectron spectra can be of the order of ± 1 eV, the difference of ~ 0.14 eV between the fourth and the last row of Table 1 for the valence band width is negligible for all practical purposes.

Let us now turn to the basis set dependence of the computed ground state properties. A close examination of the numerical results in Table 3 demonstrates that the variation of the equilibrium distance as a function of the basis set used is much larger than the changes due to lattice summations. Generally, an improvement of the basis set applied affects the equilibrium distance of the infinite chain in the same direction as for the case of the isolated molecule, although the quantitative effects are somewhat modified. While the addition of two p functions to the 8s basis reduces the equilibrium distance of the Li_2 molecule by ~ 0.2 a.u., the effect is much smaller, although still significant, in the infinite chain. The rather large change from the 8s to the 9s basis, which contains already two functions for the 2s level of the Li atom, demonstrates that for a correct description of the metallic bonding additional flexibility is needed in this region. As has been found earlier by several groups, polarization functions always compensate partly the deficiencies in the s basis.

A comparison of the isolated Li_2 molecule and the linear lithium chain shows a marked increase in the equilibrium distance by about 10%. This is in qualitative agreement with experiment, since the equilibrium distance in the body-centered Li crystal is $\sim 14\%$ larger than in Li_2. The Hartree–Fock limit value for $r_e(Li_2)$ [28] is about 0.2 a.u. larger than the experimental one. Therefore a similar effect could be expected for the Hartree–Fock limit equilibrium distance of the three-dimensional crystal, if one assumes that the influence of electron correlation on the interatomic distances does not change dramatically for these two systems.

Ab initio calculations on the Li crystal by Kumar *et al.* [23] yielded an equilibrium distance which was 20% larger than the experimental value. The authors attributed this discrepancy to the inherent deficiencies of the Hartree–Fock approach for metallic systems. On the other hand, Sperber and Calais [22] and Stoll and Preuß [5] report values much closer to experiment (see Table 4).

Although a comparison between one-dimensional and three-dimensional calculations is certainly questionable, it might give some information on the origin of this

Table 3. Equilibrium distance, force constant, and total energy per unit cell for an infinite, metallic lithium chain as a function of the basis set used

Basis set[a]	Number of neighbors	Number of k-points	r_e[a.u.]		f[mdyne/Å]		Total energy per unit cell	
6s(3, 1, 1, 1)	6	13	5.8918	(5.442)[b]	0.121	(0.220)[b]	−7.424737	(−7.426914)[c]
8s(4, 1, 1, 1, 1)	4	9	5.8902	(5.451)	0.121	(0.220)	−7.427901	(−7.430090)
8s	6	13	5.9025		0.121		−7.427920	
8s1p(p-exp =0.13)	6	13	5.8438	(5.255)	0.115	(0.247)	−7.429477	(−7.433713)
8s2p(0.5, 0.1)	6	13	5.8315	(5.241)	0.113	(0.251)	−7·429682	(−7.434270)
9s(4, 1, 1, 1, 1, 1)	4	9	5.8169	(5.398)	0.106	(0.197)	−7.428415	(−7.430764)
9s	6	13	5.8275		0.105		−7.428388	
9s	8	17	5.8304		0.105		−7.428394	
9s2p(0.5, 0.1)	4	9	5.7905	(5.264)	0.113	(0.237)	−7.430729	(−7.435217)
9s2p	6	13	5.8092		0.113		−7.430624	
9s2p	8	17	5,8139		0.113		−7.430606	
STO-3G[d]	6	13	5.9323	(5.514)	0.110	(0.202)	−7.323600	(−7.325986)
STO-3G[e]	6	13	6.7135	(6.281)	0.067	(0.122)	−7.313526	(−7.315265)

[a] See Ref. [17].

[b] Values in parentheses refer to the isolated Li_2-molecule.

[c] Values in parentheses are defined as $E_{Li(2}$.

[d] Standard basis without p-functions.

[d] Expansion of the basis used in [23].

r_e(Li–Li) a.u.	Ref.
6.99 (bcc)	[23]
7.18 (fcc)	[23]
6.05 (bcc)	[22]
5.82 (bcc)	[5]
5.74 (bcc)[a]	[29]
5.88(fcc)[a]	[29]

[a] Experimental value.

Table 4. Equilibrium distances for the lithium crystal obtained by previous *ab initio* calculations and by experiment

discrepancy. In Ref. [23] a basis set of Slater type orbitals was used, composed of a 1*s* function with standard exponents 2.69 and two 2*s* functions with exponents 3.0 and 0.5, respectively. We mimiced this basis by an STO-3G expansion [30] using the same exponents and performed also calculations with the standard STO-3G basis with exponents 2.69 and 0.65 for the 1*s* and 2*s* function, respectively. The corresponding results are shown in the two last rows of Table 3. Surprisingly a lower energy for the standard STO-3G basis was found, contrary to the result of Kumar *et al.* Moreover the extremely large difference in the equilibrium distance for both Li_2 and the infinite lithium chain, using the basis of Kumar *et al.* compared to all other basis sets used in the present work, leads us to the conclusion that their results most probably reflect the deficiency of the particular basis set chosen. Furthermore, they reported a positive Fermi energy, although it is well known that all eigenvalues of occupied states must be negative (see e.g. Ref. [31]) in a Hartree–Fock calculation. As a consequence of this result they found a width of the occupied part of the valence band of about 7.2 eV. Since from experiment a width of about 4 eV can be deduced [24], they attributed this large difference again to the

Table 5. Valence band of a linear, metallic lithium chain at the respective equilibrium geometries as a function of the basis set used and the number of neighbors taken into account. All values are given in eV

Basis set	Number of neighbors	$\varepsilon_{2s}(0)$	$\varepsilon_{\text{Fermi}}$	Width of the occupied part	Width of the unoccupied part
6*s*[a]	6	−6.31	−2.98	3.33	6.00
8*s*	4	−6.30	−3.07	3.23	6.59
8*s*	6	−6.31	−2.99	3.32	5.97
8*s*1*p*	6	−6.31	−3.13	3.18	4.93
8*s*2*p*	6	−6.32	−3.16	3.16	4.55
9*s*	8	−6.25	−2.95	3.33	6.68
9*s*2*p*	4	−6.35	−3.30	3.05	4.47
9*s*2*p*	6	−6.41	−3.20	3.21	4.56
9*s*2*p*	8	−6.23	−3.14	3.08	4.56
STO-3G[b]	6	−6.31	−2.97	3.34	6.07
STO-3G[c]	6	−6.15	−3.48	2.66	4.43

[a] For contractions see Table 3.
[b] Standard STO-3G basis set without p_z-functions.
[c] STO-3G expansion of the basis set used in Ref. [23].

inherent deficiencies of the Hartree–Fock method in metallic systems. Although there is certainly a significant systematic error in the Hartree–Fock treatment of these types of systems, due to the occurrence of nearly degenerate states the quantitative effects have not yet been assessed and have probably been overestimated in their work.

Table 5 shows the lower band edge of the linear, metallic lithium chain together with the Fermi level. One can observe that the computed results are not extremely sensitive to variations in the basis set. In the subsequent chapters we will demonstrate that this is not always the case. The width of the unoccupied part of the valence band is given only as an illustration. No direct physical significance can be attributed to these virtual levels in the framework of the Hartree–Fock picture.

4. The Linear Lithium Hydride Chain

For our model studies on a typically ionic system we chose the linear chain of lithium hydride molecules. Small clusters of lithium hydride have recently been studied by Rupp and Ahlrichs [32]. These authors found that inclusion of electron correlation leads only to a negligible correction of the order of 1 kcal/mole in the reaction energy $(\mathrm{LiH})_n + \mathrm{LiH} = (\mathrm{LiH})_{n+1}$. The lithium hydride crystal has been investigated previously at the Hartree–Fock level by Kunz and Mickish [33, 34] and by Stoll and Preuß [35]. A linear lithium hydride dimer was studied by Rychlewsky and Sabin [36]. The equilibrium geometry of $(\mathrm{LiH})_2$ has been found to be a centro-symmetric one [37, 38]. Since the linear lithium hydride chain is energetically disfavored compared to structures with higher symmetries, no comparison to dimer calculations was attempted in this work. The only other available calculation on the LiH chain has been performed using the FSGO method [39].

Pilot calculations on the $(\mathrm{LiH})_\infty$ system with two different LiH distances indicated that with increasing number of neighbors the two distances tend to become equal. While in second neighbors interactions the difference is still 0.04 a.u., inclusion of the third neighbors leads to a difference of only 0.02 a.u. This result demonstrates that chemical bonding in the lithium hydride chain is completely different from the case of the hydrogen fluoride chain, where a hydrogen bonded, nonequidistant molecular chain is found to have the lowest energy [9]. Consequently, for all further investigations only the equidistant lithium hydride chain was treated. As in the previously discussed case of the lithium chain extensive investigations on the basis set dependence and of the effect of truncating the lattice sums have been performed.

In Table 6 the resulting equilibrium geometries, force constants, Mulliken populations, the total energy per unit cell and the corresponding stabilization energy per unit cell are shown. For completeness the values for the isolated molecule are given as well. In Fig. 1 the 2σ-valence band obtained in sixth neighbor's interactions using the 8/4 and 8, 1/4, 1 basis is depicted. Table 7 shows the variation of the computed band structure with different number of neighbors and different basis sets. The variation of the computed properties with increasing number of k-points

Table 6. Equilibrium distance, force constant, Mulliken population on the hydrogen atom, total energy per unit cell and stabilization energy per unit cell for an equidistant, infinite lithium hydride chain as a function of the basis set applied and the number of neighbors taken into account

Basis set[a]	Number of neighbors	r_{LiH} [a.u.]	f [mdyne/A]	q_{H}	E/cell [a.u.]	E/cell $- E_{\mathrm{LiH}}$ [kcal/mole]
7/3 (4/2)	6	3.207 (3.082)[b]	1.558 (1.026)[b]	1.776 (1.579)[b]	−8.031016	−48.40
7, 1/3, 1[c]	6	3.168 (3.001)	1.573 (1.218)	1.721 (1.638)	−8.037900	−38.48
8/4 (5, 3)	2	3.262 (3.109)	1.326 (0.947)	1.801 (1.650)	−8.032228	−39.86
8/4	3	3.253	1.346	1.833	−8.033735	−40.81
8/4	4	3.248	1.356	1.845	−8.034486	−41.28
8/4	5	3.245	1.361	1.852	−8.034896	−41.54
8/4	6	3.243	1.364	1.856	−8.035136	−41.69
8, 1/4, 1	2	3.194 (3.018)	1.412 (1.154)	1.735 (1.733)	−8.039707	−35.77
8, 1/4, 1	3	3.191	1.427	1.767	−8.040752	−36.43
8, 1/4, 1	4	3.190	1.435	1.781	−8.041335	−36.79
8, 1/4, 1	5	3.188	1.440	1.787	−8.041667	−37.00
8, 1/4, 1	6	3.187	1.442	1.792	−8.041868	−37.13
8/5 (5/4)	6	3.239 (3.113)	1.286 (0.912)	1.903 (1.685)	−8.035514	−41.40
8, 1/5, 1	6	3.188 (3.027)	1.426 (1.130)	1.832 (1.788)	−8.042560	−34.68

[a] See Refs. [17] and [18].

[b] Values in parentheses refer to the LiH molecule.

[a] See Refs. [17] and [18].

[b] Values in parentheses refer to the LiH molecule.

[c] $p_{\mathrm{Li}}=0.5$, $p_{\mathrm{H}}=0.2$.

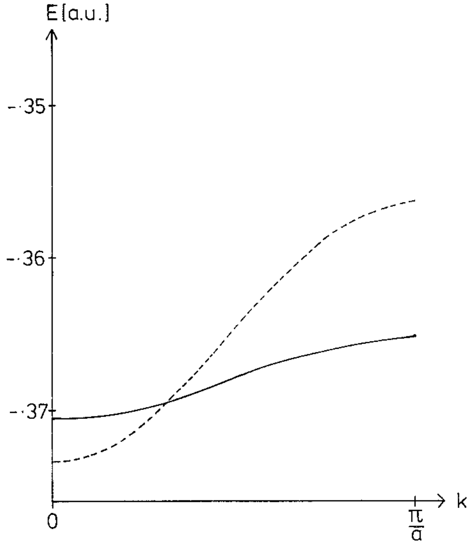

Fig. 1. 2σ-valence band of a linear lithium hydride chain with sixth neighbor's interactions. The full line results from a calculation with the 8, 1/4, 1 basis set, the broken line was obtained with the 8/4 basis

was found to be insignificant, provided their number exceeds the absolute minimum needed.

From these results a number of conclusions can be drawn. The equilibrium distance in the infinite chain is larger than for the isolated molecule, similar to the case of the isolated lithium chain, although this effect was much more pronounced in the former case. The experimental bond distance in the LiH crystal (3.87 a.u.) is much larger than our computed equilibrium distance for the linear chain. This is not too surprising since the isotropic, cubic lithium hydride crystal does not have much in common with the extremely anisotropic, linear structure. Due to problems with

Table 7. Band structure of the linear lithium hydride chain with different basis sets and with different number of neighbors. All values in a.u.

Basis set	Number of neighbors	$\varepsilon_{1\sigma}(0)$	$\varepsilon_{1\sigma}(\pi)$	$\Delta_{1\sigma}$	$\varepsilon_{2\sigma}(0)$	$\varepsilon_{2\sigma}(\pi)$	$\Delta_{2\sigma}$
7/3[a]	6	−2.40666	−2.40638	0.00028	−0.37123	−0.35240	0.01883
7, 1/3, 1	6	−2.39306	−2.39272	0.00034	−0.36919	−0.36392	0.00527
8/4	2	−2.42717	−2.42695	0.00022	−0.38071	−0.36070	0.02001
8/4	3	−2.41790	−2.41768	0.00022	−0.37504	−0.35652	0.01852
8/4	4	−2.41424	−2.41401	0.00023	−0.37314	−0.35551	0.01763
8/4	5	−2.41241	−2.41218	0.00023	−0.37247	−0.35512	0.01735
8/4	6	−2.41135	−2.41111	0.00024	−0.37208	−0.35468	0.01722
8, 1/4, 1	4	−2.39892	−2.39861	0.00031	−0.37324	−0.36773	0.00551
8, 1/4, 1	5	−2.39685	−2.39654	0.00031	−0.37152	−0.36663	0.00489
8, 1/4, 1	6	−2.39571	−2.39540	0.00031	−0.37091	−0.36611	0.00480
8/5	6	−2.41124	−2.41103	0.00021	−0.37157	−0.35407	0.01750
8, 1/5, 1	6	−2.39559	−2.39527	0.00032	−0.37093	−0.36618	0.00475

[a] See Table 6.

near linear dependencies, already mentioned in chapter 2, calculations with first neighbor's interactions could not be performed, hence the convergence could only be studied starting from second neighbors. Again, as in the previous chapter, variations in the computed properties due to changes in the basis set are much more pronounced than changes due to the extension of lattice summations. Increasing the number of *s* type functions leads to an increase in the equilibrium distance, whereas inclusion of polarization functions has the opposite effect. These trends could already be guessed from the results on the isolated LiH molecule. The ionicity of the LiH bond is increased in the infinite chain. Inclusion of the sixth neighbors is sufficient to obtain the equilibrium distance to within ~0.002 a.u.

Turning to the total energies per unit cell it is important to note that already second neighbor's interactions give a value reasonably close to the ones obtained from more elaborate lattice summations. This is due to the fact that in the CO approach the translationally symmetric potential is essentially already correct for finite neighbor's interactions, whereas the situation is different in cluster type calculations, where edge effects are far more important. Nevertheless for a more accurate evaluation of the stabilization energy per unit cell one has to take into account the Coulomb field of the further neighbors.

Rather drastic changes have been found in the band width of the 2σ-band, when the basis was improved by the inclusion of a polarization set. Although the total band width as such is very small indeed, a relative change by roughly a factor of four seems to be significant and shows the necessity of using extended basis sets for the proper calculation of band structures. The effect of including further neighbors can be described as an almost uniform shift of the bands on the energy scale.

5. The Beryllium Hydride Polymer $(BeH_2)_x$

As a third example for our model studies the beryllium hydride polymer was treated (see Fig. 2). Because of experimental difficulties the structure of solid BeH_2 has not yet been determined. It has been suggested [40] that a hydrogen-bonded polymer might be a conceivable structure which could exist in solid BeH_2.

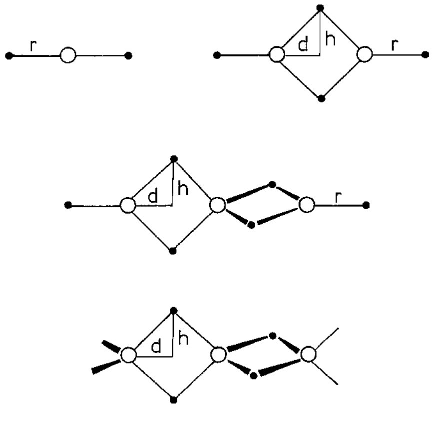

Fig. 2. Geometries of small beryllium hydride clusters and the infinite $(BeH_2)_x$ polymer. Large open circles correspond to the Be atom, small full circles to the H atom

Table 8. Equilibrium geometries and total energies of BeH_2 with various basis sets. All values in a.u.

Basis set	r_e	Total energy
8/4 (4, 1, 1, 1, 1/2, 1, 1)[a]	2.602	−15.656763
8, 1/4 (*p*-exp. =0.4)	2.523	−15.748882
8, 2/4 (*p*-exp.: 1, 6, 0.3)	2.520	−15.759931
8, 2/4, 1 (p_H=0.52)	2.516	−15.765037
7/4[b]	2.592	−15.655003
7, 1/4	2.518	−15.746980

[a] See Refs. [17] and [18].

[b] Originating from the 8*s* basis by omitting the function with smallest exponent.

Recent quantum mechanical calculations supported this point of view [41]. Chainlike structures were reported to be energetically more favored than cyclic arrangements. A rather high cohesion energy of −48 kcal/mole for the BeH_2 crystal has been estimated earlier [42]. In Ref. [41] the extreme sensitivity to changes in the basis set of the stabilization energy for the reaction $2\,BeH_2 \rightarrow Be_2H_4$ has already been noted. Our calculations confirmed this result. In Tables 8 and 9 the equilibrium geometries and total energies of BeH_2 and the dimer Be_2H_4 obtained with different basis sets are collected. For BeH_2 only the linear structure was considered, while Be_2H_4 was assumed to have D_{2h} symmetry. One can easily recognize that the equilibrium geometry changes drastically on inclusion of one *p* function on Be. This effect is especially large in the dimer. A further improvement of the basis set has only minor consequences for the equilibrium geometry (a slight reduction of the terminal Be–H distance), whereas the stabilization energy of the dimer is still increasing, and it seems that it has not yet converged. Hence, compared to Ref. [41], we find a slightly larger stabilization energy on the SCF level, which is due to the more complete geometry optimization in this work. The *p* functions on the hydrogen atoms have also a non-negligible effect. Additionally the geometry of Be_3H_6 was partly optimized with the 7, 1/4 basis using the same geometrical parameters as in the case of Be_2H_4 and assuming a D_{2d} configuration,

Table 9. Equilibrium geometries, total energies and stabilization energies of Be_2H_4 and Be_3H_6 with various basis sets

	Basis set[a]	d^b [a.u.]	h [a.u.]	r [a.u.]	Total energy [a.u.]	$E_{Be_2H_4}-2E_{BeH_2}$ [kcal/mole]	$E_{Be_3H_6}-(E_{Be_2H_4}+E_{BeH_2})$ [kcal/mole]
Be_2H_4	8/4	2.330	1.858	2.600	−31.319542	−3.77	–
	8, 1/4	1.947	2.002	2.525	−31.526726	−18.20	–
	8, 2/4	1.949	2.004	2.519	−31.552513	−20.59	–
	8, 2/4, 1	1.951	1.999	2.514	−31.566378	−22.72	–
	7/4	2.352	1.898	2.582	−31.313641	−2.26	–
	7, 1/4	1.946	2.000	2.515	−31.524193	−18.96	–
Be_3H_6	7, 1/4	1.944	2.012	2.509	−47.314818	–	−27.37
	8, 2/4, 1	1.944[c]	2.012	2.509	−47.378329	–	−29.46

[a] See Table 8.

[b] For the definition of the geometrical parameters see Fig. 2.

[c] Not optimized, same geometry as with 7, 1/4 basis.

Table 10. Equilibrium geometry and total energy of the beryllium hydride polymer as a function of basis set and number of neighbors. All values in a.u.

Basis set[a]	Number of neighbors	d^{b}	h	E/cell
7/4	1	2.202	1.938	−31.298179
7/4	2	2.217	1.927	−31.310883
7/4	3	2.219	1.928	−31.315763
7, 1/4	2	1.898	2.024	−31.577967
7, 1/4	3	1.901	2.025	−31.577951

[a] See Table 8.
[b] See Fig. 2.

thereby neglecting that in the Be–H–Be bridged bond, the two Be–H distances are no longer exactly equal. The resulting minimum geometry was then recomputed in the 8, 2/4, 1 basis, leading to a stabilization energy for $Be_2H_4 + BeH_2 \rightarrow Be_3H_6$ of 29.5 kcal/mole, which is about 2.5 kcal/mole larger than found in Ref. [41].

In the case of the $(BeH_2)_x$ polymer difficulties due to near-linear dependencies were encountered if the 8/4 basis was applied. To overcome this problem the 8*s* basis on beryllium was reduced to 7*s* by omitting the function with smallest exponent. The effect of this procedure has been tested on BeH_2 and Be_2H_4 (see Tables 8 and 9), and was found to be almost negligible. The structure of the beryllium hydride polymer was optimized with respect to the parameters d and h (see Fig. 2) with various neighbors in the 7/4 and 7, 1/4 basis. The corresponding results are shown in Table 10. The enormous effect of the polarization function on the equilibrium geometry parallels the one for the oligomers. The difference in the convergence behavior of the total energy per unit cell with and without a p set on beryllium may probably be attributed to the different polarity observed. Mulliken population analysis leads to Be(2.502) and H(1.749) with the 7/4 basis, whereas with the (7, 1/4) basis one obtains Be(3.191) and H(1.404). Table 11 gives a survey of equilibrium geometries and stabilization energies for the reactions $(BeH_2)_n + BeH_2 \rightarrow (BeH_2)_{n+1} + \Delta E$, using the 7, 1/4 basis.

Surprisingly enough, a slightly lower stabilization energy per BeH_2 was found in the infinite chain than for the reaction $Be_2H_4 + BeH_2 \rightarrow Be_3H_6$. Although this

Table 11. Equilibrium geometries and stabilization energies for the reactions $(BeH_2)_n + BeH_2 \rightarrow (BeH_2)_{n+1} + \Delta E$, using the 7, 1/4 basis set

	d^{a}	h	r	E[kcal/mole]
BeH_2	–	–	2.518	–
Be_2H_4	1.946	2.000	2.515	−18.96
Be_3H_6	1.944	2.012	2.509	−27.37
Be_4H_8	1.944[b]	2.012	2.509	−25.86
$(BeH_2)_x$[c]	1.901	2.025	–	−26.36

[a] Geometry given in a.u.
[b] Assumed geometry.
[c] With third neighbor's interactions.

could in principle be traced back to a not yet sufficiently converged total energy per unit cell, we find the same effect for the reaction $Be_3H_6 + BeH_2 \rightarrow Be_4H_8$. Further geometry optimization in Be_4H_8 can certainly not change the picture. No explanation could be found for this puzzling result. Generally, one can observe that $(BeH_2)_x$ seems to be a case where cluster calculations with a small number n yield results which are quite close to the ones for the infinite chain. A similar result has been suspected in Ref. [41]. This is probably due to the fact that all these clusters with $n = 2, 3, \ldots$ are symmetric with respect to edge effects, contrary to the case of a chain of polar AB molecules, as e.g. $(LiH)_\infty$ or $(HF)_\infty$. The largest difference in geometrical parameters between Be_2H_4 and $(BeH_2)_x$ occurs for the Be–Be distance, which is contracted by about 0.1 a.u. in the infinite chain. In Fig. 3 the band structure of the beryllium hydride polymer is shown for the case of third neighbor's interactions. The valence bands are given for the equilibrium geometry using the 7, 1/4 basis. For comparison results without the polarization function are given as well. The geometry was identical in both cases. The highest valence band is degenerate. As in the case of the lithium hydride chain a rather drastic effect can be observed. Inclusion of a set of p functions on Be results in a change of the band widths by about a factor of two. Since p functions on hydrogen were not included, one can expect a further change if still more extended basis sets are used. The inclusion of further neighbors manifests itself in a uniform shift on the energy scale, similar to the case previously treated.

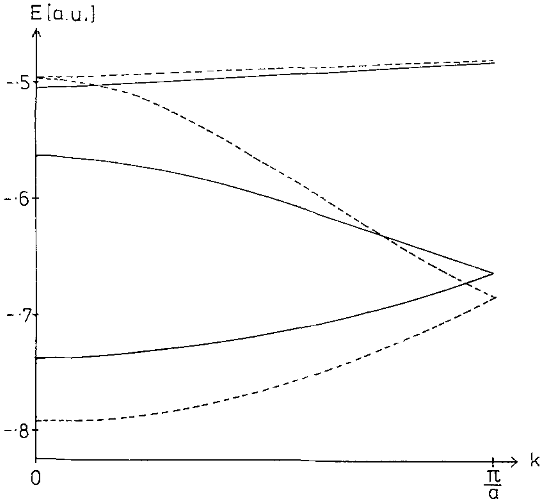

Fig. 3. Band structure of the beryllium hydride polymer with third neighbor's interactions. Full lines result from a calculation with the 7, 1/4 basis set, the broken lines were obtained with the 7/4 basis

6. Conclusions

A series of systematic investigations has been presented in this work which demonstrates that the CO method is a very useful tool for the evaluation of ground state properties of polymers, including geometries and force constants. One can expect that this approach will work equally well in the case of two- and three-dimensional aggregates. Yet, for a more quantitative description it is of primary importance, as in the case of molecules, to use more extended basis sets. Band structures turned out to be extremely sensitive. Errors of more than 100% can be obtained if the basis set applied is not sufficiently flexible in the valence region. It is tempting to try to establish an order concerning the relative importance of the convergence of the various expansions, which have been discussed in this work. As a simple rule one could say that convergence with respect to the basis set is crucial. Next important is a correct treatment of lattice sums, whereas the number of k-points has only a minor influence. This relative ordering of effects has been found in all examples studied. As a consequence of the near-linear dependencies the first two convergence problems are intimately connected. The use of larger basis sets induces the necessity to include further neighbors. It is this specific feature which calls for an approximate treatment of the influence of more distant neighbors. In a first step a sufficiently accurate description of the unit cell and the chemical bonding between cells has to be reached. The remaining bulk effects could for example be taken into account by electrostatic approximations or by some sort of integral approximations. Work along these lines is in progress in our laboratory.

Acknowledgement. The author wants to express his thanks to Prof. P. Schuster for his continuing interest in this work and to Dr. H. Lischka for numerous helpful discussions. Financial support by the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung" (Project Nr. 2756) and generous supply with computer time by the "Interuniversitäres Rechenzentrum, Wien" are gratefully acknowledged.

References

1. del Re, G., Ladik, J., Biczo, G.: Phys. Rev. **155**, 997 (1967)
2. André, J. M., Gouverneur, L., Leroy, G.: Intern. J. Quantum. Chem. **1**, 451 (1967)
3. Harris, F. E., Kumar, L., Monkhorst, H. J.: Phys. Rev. **B7**, 2850 (1973)
4. Euwema, R. N., Wilhite, D. L., Surratt, G. T.: Phys. Rev. **B7**, 818 (1973)
5. Stoll, H., Preuß, H.: Intern. J. Quantum Chem. **9**, 775 (1975)
6. Kunz, A. B.: Phys. Rev. **B7**, 5369 (1973)
7. Schaefer III, H. F.: The electronic structure of atoms and molecules. New York: Addison-Wesley 1972
8. Ahlrichs, R., Lischka, H., Zurawski, B., Kutzelnigg, W.: J. Chem. Phys. **63**, 4685 (1975)
9. Karpfen, A., Schuster, P.: Chem. Phys. Letters **44**, 459 (1976)
10. André, J. M., Leroy, G.: Chem. Phys. Letters **5**, 71 (1970)
11. André, J. M., Leroy, G.: Ann. Soc. Sci. Bruxelles Ser. 1 **84**, 133 (1970)
12. Kertesz, M., Koller, J., Azman, A.: J. Chem. Phys. **67**, 1180 (1977)
13. Kertesz, M., Koller, J., Azman, A., Suhai, S.: Phys. Letters **55A**, 107 (1975)
14. Merkel, C., Ladik, J.: Phys. Letters **56A**, 395 (1976)
15. Suhai, S., Ladik, J.: Solid State Comm. **22**, 227 (1977)
16. Ladik, J.: in: Electronic structure of polymers and molecular crystals, p. 23, André, J. M., Ladik, J. Eds. New York: Plenum Press 1975
17. Huzinaga, S.: Approximate atomic functions I. University of Alberta, Canada 1971
18. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
19. Löwdin, P. O.: J. Appl. Phys. Suppl. **33**, 251 (1962)
20. O'Keefe, P. M., Goddard III, W. A.: Phys. Rev. Letters **23**, 300 (1969)

21. Goddard, W. A., O'Keefe, P. M.: in: Computational methods in band theory, p. 542, Marcus, P. M., Janak, J. F., Williams, A. R. Eds. New York: Plenum Press 1971
22. Calais, J. L., Sperber, G.: Intern. J. Quantum Chem. **7**, 501 (1973)
23. Kumar, L., Monkhorst, H. J., Harris, F. E.: Phys. Rev. **B9**, 4084 (1974)
24. Kumar, L., Monkhorst, H. J.: J. Phys. **F4**, 1135 (1974)
25. Kertesz, M., Koller, J., Zakrajsek, E., Azman, A.: Z. Naturforsch. **32a**, 453 (1977)
26. Delhalle, J.: Intern. J. Quantum Chem. **8**, 201 (1974)
27. Koopmans, T.: Physica **1**, 104 (1933)
28. Das, G., Wahl, A. C.: J. Chem. Phys. **44**, 87 (1966)
29. Slater, J. C.: Quantum theory of molecules and solids, Vol. 2, Appendix 1. New York: McGraw Hill 1965
30. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
31. Ahlrichs, R.: Chem. Phys. Letters **34**, 570 (1975)
32. Rupp, M., Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **46**, 117 (1977)
33. Kunz, A. B., Mickish, D. J.: J. Phys. **C6**, L83 (1973)
34. Kunz, A. B., Mickish, D. J.: Phys. Rev. **B11**, 1700 (1975)
35. Stoll, H., Preuß, H.: Theoret. Chim. Acta (Berl.) **46**, 11 (1977)
36. Rychlewski, J., Sabin, J. R.: Chem. Phys. Letters **37**, 180 (1976)
37. Kollman, P., Bender, C. F., Rothenberg, S.: J. Am. Chem. Soc. **94**, 8016 (1972)
38. Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **35**, 59 (1974)
39. Delhalle, J., André, J. M., Demanet, Ch., Brédas, J. L.: Chem. Phys. Letters **54**, 186 (1978)
40. Wiberg, E., Bauer, R.: Z. Naturforsch. **6b**, 171 (1951)
41. Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **17**, 348 (1970)
42. Ahlrichs, R., Kutzelnigg, W.: Theoret. Chim. Acta (Berl.) **10**, 377 (1968)
43. Kertesz, M.: Acta Phys. Hung. **41**, 107 (1976)
44. Kertesz, M., Koller, J., Azman, A.: Z. Naturforsch. **33a**, 249 (1978)

Received April 19, 1978/June 19, 1978