

Theoretical Study of Be_N Linear Chains: Optimized Geometries and Harmonic Frequencies

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Abstract: The electronic structure of linear beryllium chains has been theoretically studied at an *ab initio* level. By using a CAS-SCF approach, geometries have been optimized and harmonic frequencies computed. The optimized geometries present almost equal bond lengths, while all the harmonic frequencies are real. This fact indicates the presence of a local minimum, at this level of theory, having a linear geometry. The energy splitting between the singlet ground state, $^1\Sigma_g$, and the quasi-degenerated excited triplet, $^3\Sigma_u$, has been computed at CAS-SCF and MR-CI level. It was found that the splitting goes exponentially to zero as the number of atoms in the chain is increased.

1. Introduction

The interest on linear surface-deposited atomic structures has grown enormously in the last years, particularly since it became possible to synthesize one-dimensional electron systems at stepped surfaces.^{1–5} A common feature of these systems is the presence of edge orbitals corresponding to the “surface states” (in a one-electron formalism) introduced by Tamm and Shockley long ago.⁶ Edge effects, for instance, have been predicted in graphene nanoribbons,^{7,8} and this can produce a large variety of interesting electric and magnetic behaviors.⁹ In one-dimensional systems, these states are also called “end states” and have been detected, for instance, in gold atomic chains deposited on silicon surfaces.⁵

In the case of the phenomenological Hückel Hamiltonian, it has been shown that edge orbitals can be present, under particular conditions, at the extremities of a bond-alternating linear polyene.¹⁰ These edge orbitals, that have quasi-degenerate energies, present exponentially decaying amplitudes in the inner atoms of the chain. In recent works, a similar behavior has been theoretically predicted for the case of linear beryllium chains treated at an *ab initio* level.^{11,12}

In particular, it has been shown that, for internuclear distances close to the equilibrium structure, two partially filled edge orbitals localize at the chain ends. This gives rise to two low-lying quasi-degenerated states, a singlet ground state, $^1\Sigma_g$, and a triplet, $^3\Sigma_u$. Their energy splitting goes exponentially to zero as the number of atoms in the chain is increased.

These calculations were performed by assuming equally spaced linear arrangements for the chain geometries. Therefore, it is interesting to perform separate optimization of all the bond distances, in order to see if the system remains stable under these conditions. Moreover, if this is the case, one must characterize the nature of the stationary point obtained through geometry optimization. If all the second derivatives are positive, i.e., the harmonic frequencies are real (and positive), the stationary point is a local minimum on the Potential Energy Surface (PES) of the system. In this case, it is in principle possible to produce this molecular species, although its stability is related to dynamical and thermodynamical aspects. For these reasons, in the present work we present a CAS-SCF investigation of the geometrical structure of these systems by relaxing the equal-bond constrain. It turns out that the optimized geometries are very close to the constrained-minimum ones. Moreover, all the

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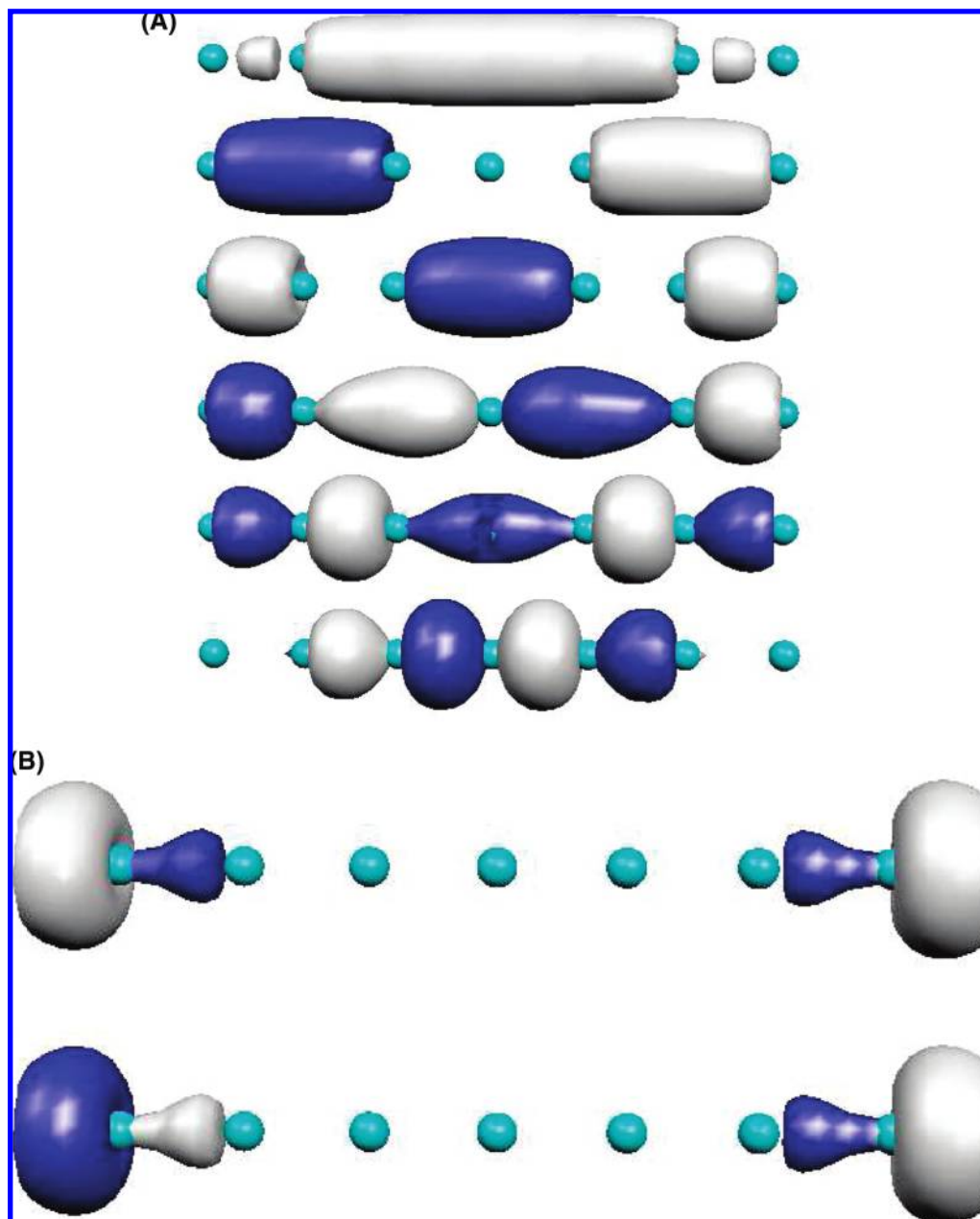


Figure 1. Valence CAS-SCF orbitals for the Be₇ chain: occupied orbitals (a) and active orbitals (b).

harmonic frequencies of these systems are real and positive, which means that, at this level of description, the optimized linear structures are local minima on the Potential-Energy Surfaces (PES) of the Be_N chains.

This article is organized as follows: in the next section, Section 2, the electronic structure of beryllium chains is considered, showing how a linear disposition of the atoms can lead to relatively stable electronic states; in Section 3, the theoretical framework of the investigation is described; in Section 4, the optimized geometries, and the harmonic frequencies computed at this geometry, are presented and discussed; the singlet–triplet energy splitting is also investigated, showing that these chains have an antiferromagnetic behavior, with an exponentially decaying coupling constant as a function of the number of atoms; finally, in Section 5, some conclusions are drawn, and the problem of the existence and stability of these structures is addressed.

Table 1. Orbital Symmetry, Energies (hartree), and Occupation Numbers of the Occupied-Valence and Active CAS-SCF Orbitals for Be₇, at the Equilibrium Geometry^a

orbital	symmetry	energy	occupation
1	5σ _g	−0.4123	2.000000
2	4σ _u	−0.4011	2.000000
3	6σ _g	−0.3765	2.000000
4	5σ _u	−0.3431	2.000000
5	7σ _g	−0.3024	2.000000
6	6σ _u	−0.2592	2.000000
7	8σ _g	−0.0738	1.004429
8	7σ _u	−0.0729	0.995571

^a The orbitals are shown in Figure 1.

2. The Electronic Structure of Beryllium Chains

Beryllium is a metallic divalent element. The isolated atom has a closed-shell 1s²2s² electronic configuration, so the

Table 2. Equilibrium Bond Distances (bohr) as a Function of the Chain Length N^a

N	1	2	3	4	5	6
2	4.319					
3	4.115					
4		4.086				
5	4.094	4.105				
6	4.102	4.097	4.109			
7	4.106	4.099	4.110			
8	4.109	4.108	4.100	4.110		
9	4.111	4.108	4.100	4.111		
10	4.113	4.112	4.109	4.101	4.111	
11	4.114	4.113	4.109	4.101	4.111	
12	4.115	4.114	4.113	4.109	4.101	4.111
13	4.115	4.115	4.113	4.109	4.101	4.111

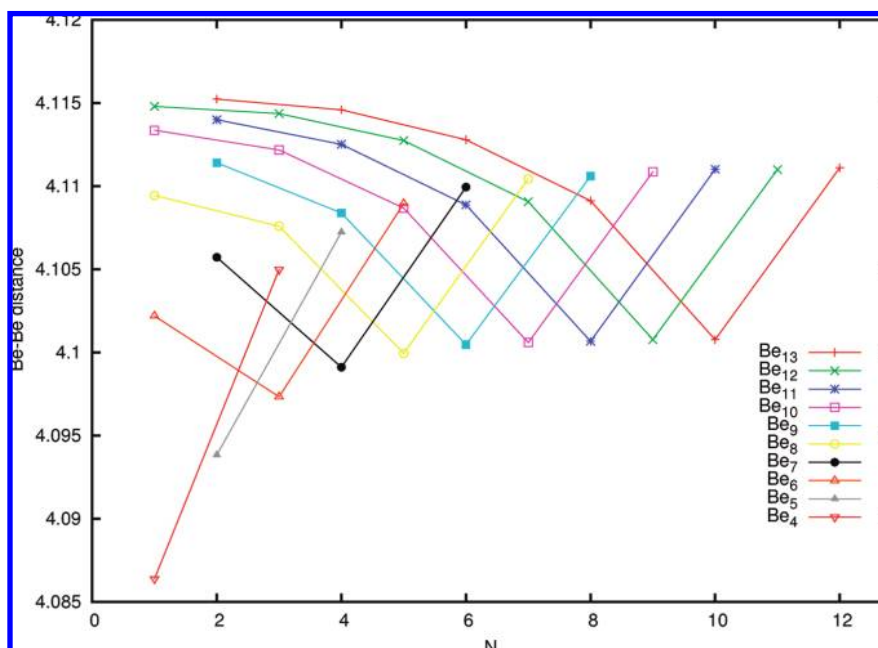
^a Bond 1 indicates the central bond in the case of even N or the two central bonds for N odd and so on.

electronic structure of this element is somewhat reminiscent of a rare gas. For this reason, this species is not particularly reactive. In fact, beryllium has a relatively large Ionization Potential (IP), while the isolated atom does not admit any stable anionic state. In particular, beryllium IP is larger than the IP of the element immediately following in the same period (boron), a fact that is not a common feature on the Periodic Table. However, the empty $2p$ orbitals are close in energy to the occupied $2s$ one.¹³ For this reason, and having two valence electrons only, beryllium is able to form at most two molecular bonds that are colinear. This is the case of the well-known species beryllium hydride (BeH_2) and the similar, although less studied, Be_nH_2 linear structures.¹⁴

Let us consider the case of a linear arrangement of N beryllium atoms, and let us take, for the sake of definiteness, the z axis as the chain direction. The symmetry group of the system is assumed to be $D_{\infty h}$ (of course, one has to verify this assumption in the course of the investigation). In particular, the orbitals will be labeled by g and u , according to their symmetry property with respect to the molecule-center of inversion.

A total of $N - 1$ Be–Be bonds are formed between neighboring atomic pairs. The bonds are the result of additive combinations of two sp_z hybrids, each one coming from one of the two atoms participating in the bond. These $N - 1$ bonds are able to host $2N - 2$ out of the $2N$ valence electrons of the system. The two remaining valence electrons can be placed in the last two valence σ orbitals, a σ_g and a σ_u . (The π valence orbitals are much higher in energy, and they do not play any important role in the qualitative description of the low-lying states at least for longer chains, as discussed in Computational Details section). They are obtained as linear combinations of the two outer sp_z hybrid bonds, one on each terminal beryllium atom. Because of their position in the chain, these external hybrids are called “edge”, or “end”, orbitals. If the chain is composed of several atoms, and considering that the optimum Be–Be distance in these structures is between four and five bohr, the two edge orbitals are quite separated, and therefore quasi degenerate. The lowest energy arrangement of the two electrons into the two orbitals is therefore, in a localized picture, one electron in each edge orbital. In terms of the delocalized symmetry orbitals, they correspond to the two configurations $(1)/(\sqrt{2})(\sigma_g\bar{\sigma}_g - \sigma_u\bar{\sigma}_u)$ (a singlet Σ_g) and $(1)/(\sqrt{2})(\sigma_g\bar{\sigma}_u + \sigma_u\bar{\sigma}_g)$ (a triplet Σ_u).

As far as the two edge orbitals, and the two corresponding electrons, are concerned, the situation is formally very much similar to the case of a stretched hydrogen molecule. Also in this case a singlet and a triplet form a manifold of degenerate states at long distance. The analogy can be pushed further, and in the case of beryllium chains one could consider the two low-lying ionic singlets arising from the double occupation of the edge orbitals, $(1)/(\sqrt{2})(\sigma_g\bar{\sigma}_u - \sigma_u\bar{\sigma}_g)$ and $(1)/(\sqrt{2})(\sigma_g\bar{\sigma}_g + \sigma_u\bar{\sigma}_u)$. However, these “ionic” states are likely to play an important role only in presence of a longitudinal electric field, and they will be the subject of future investigations.

**Figure 2.** Bond lengths of different chains Be_N , from Be_4 to Be_{13} . Bond lengths in bohr.

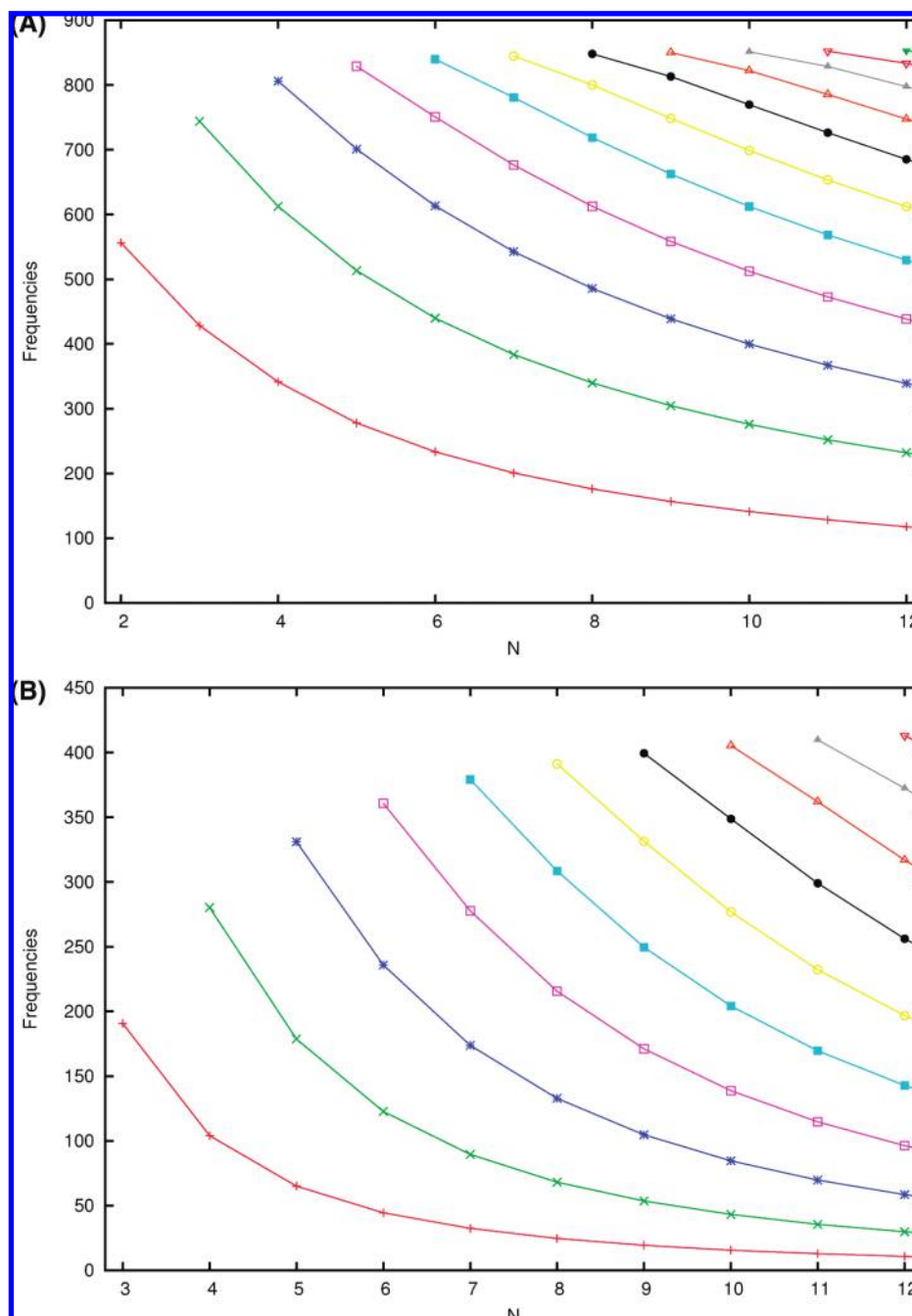


Figure 3. Harmonic frequencies for Be_N (each curve representing a different normal mode): stretching, from Be₂ to Be₁₃ (a) and bending, from Be₃ to Be₁₃ (b). Frequencies are in cm⁻¹.

3. Computational Details

In the course of the present investigation, a $D_{\infty h}$ symmetry has been assumed for the chain. However, for practical reasons, only abelian groups can be treated by most *ab initio* packages, so the actual calculation was performed in the D_{2h} abelian subgroup. Notice that, in principle, the linear chain could have a lower $C_{\infty v}$ symmetry. However, the fact that all the harmonic frequencies associated with the equilibrium geometry are real and positive excludes this possibility.

An ANO-type basis set was chosen as atomic orbitals, with the largest recommended contraction, $6s4p3d2f$.¹⁵ Due to the multireference nature of the wave function at equilibrium (two Slater determinants having virtually identical weights), the SCF wave function is not able to give a correct

description of the system. It is the CAS-SCF(2/2) description that gives the simplest qualitatively correct wave function. With this simple description we do not consider the influence of the π orbitals. The validity of this approximation can be assessed by analyzing the valence CAS-SCF of short chains. In particular the (per electron) π occupation goes from 0.06495 for the Be atom to 0.05469 for the dimer and 0.03199 for the tetramer. This fact clearly indicates a tendency toward a reduction of the π influence already evident in the dimer with respect to the isolated atom. Therefore, although π orbitals are crucial to correctly describe the dissociation of the Be₂, their influence becomes less important for longer chains, that are the main object of this investigation. The equilibrium geometries for the singlets and

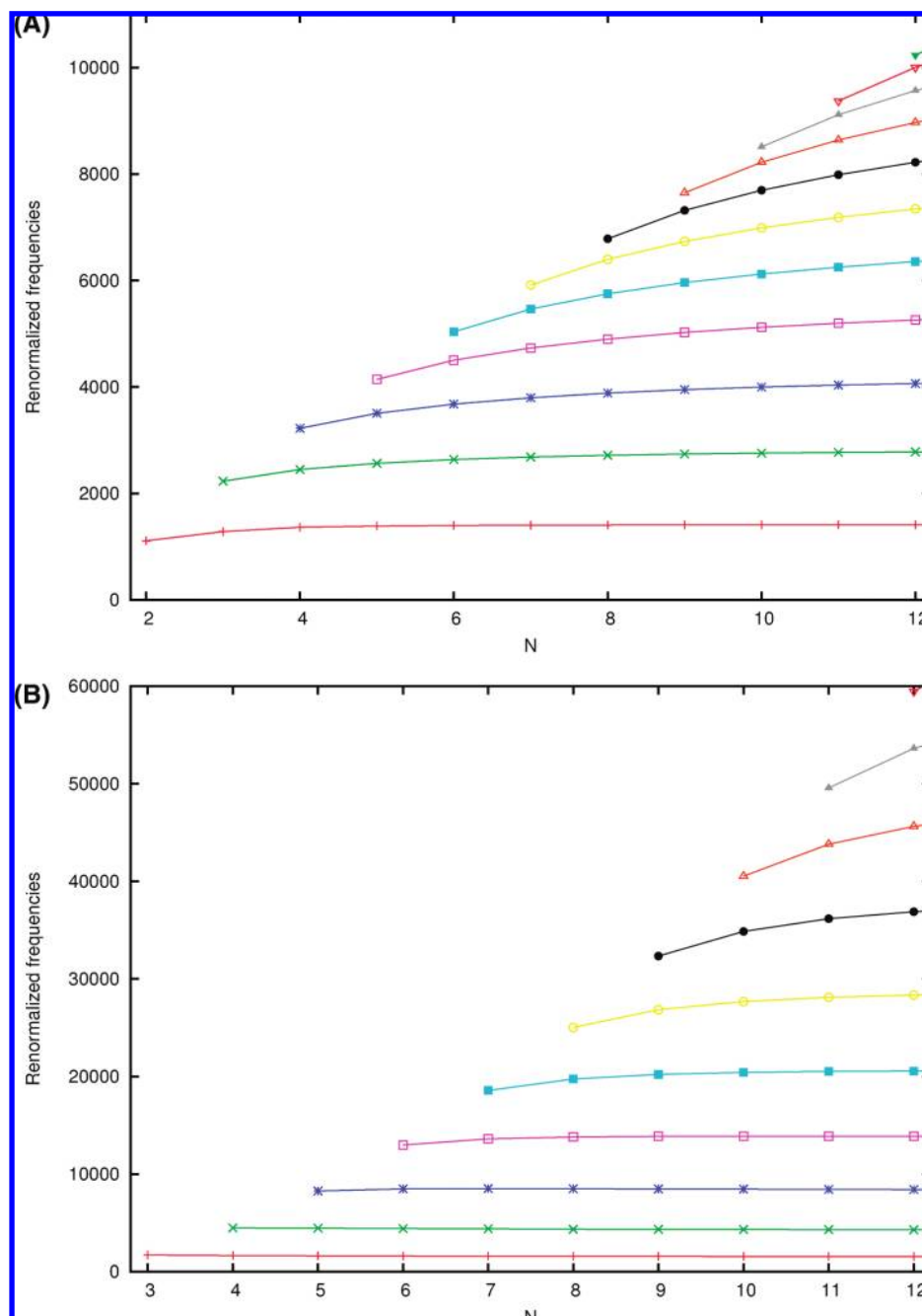


Figure 4. Renormalized harmonic frequencies for Be_N (each curve representing a different normal mode): stretching divided by N (a) and bendings divided by N^2 (b). Frequencies are in cm^{-1} .

the triplets, by imposing a linear constrain, were obtained at this level. The harmonic frequencies were then numerically computed at the equilibrium geometry for each chain. All the calculations presented in this study were obtained by using the MOLPRO¹⁶ and DALTON¹⁷ packages.

At the equilibrium geometry, singlet and triplet energies were obtained through a state-averaged CAS-SCF(2/2) calculation.^{18–20} The state-averaged orbitals were then used in the CI calculations. The CI description introduces the effects of the dynamical correlation. Although, in particular for the longest chains, total energies computed by using this method suffer for the lack of size consistency, singlet–triplet splittings are certainly much less affected. The CI calculations

reported in this work are of the internally contracted type^{21,22} and were obtained by using the MOLPRO chain.¹⁶

In all CI calculations, the $1s$ orbitals were kept doubly occupied and frozen at the CAS-SCF(2/2) level.

4. Results and Discussion

We studied linear chains containing N beryllium atoms for several values of N . The behavior of these systems while permitting independent bond-length relaxations has been investigated. It turns out that, at equilibrium, the different bond lengths coincide within a few percent. In other words, the optimized geometries are very close to the equal-bond minimum geometries investigated in previous studies.

Table 3. CAS-SCF and MR-CI Absolute Energies (hartree) for the Singlet and Triplet State for Different Beryllium Chains, at the CAS-SCF Optimized Geometry^a

<i>N</i>	MR-CI _{av} (T)	MR-CI _{av} (S)	CAS-SCF _{av} (T)	CAS-SCF _{av} (S)	CAS-SCF _{ss} (S)	RHF-SCF
2	-29.200974	-29.233715	-29.143642	-29.164091	-29.165722	-29.128752
3	-43.861856	-43.867080	-43.762741	-43.765410	-43.765580	-43.689933
4	-58.512805	-58.513587	-58.375529	-58.375899	-58.375916	-58.269425
5	-73.160347	-73.160466	-72.987399	-72.987451	-72.987453	-72.862037
6	-87.805814	-87.805836	-87.599010	-87.599018	-87.599019	-87.463211
7	-102.449702	-102.449709	-102.210526	-102.210527	-102.210527	-102.068880
8	-117.092274	-117.092278	-116.821995	-116.821995	-116.821995	-116.676827
9	-131.733710	-131.733713	-131.433440	-131.433440	-131.433440	-131.285896
10	-146.374143	-146.374145	-146.044870	-146.044870	-146.044870	-145.895630
11	-161.013680	-161.013683	-160.656291	-160.656291	-160.656291	-160.505732
12			-175.267707	-175.267707	-175.267707	-175.116102
13			-189.879119	-189.879119	-189.879119	-189.726639

^a The geometry was optimized at a state-specific CAS-SCF level for the singlet (CAS-SCF_{ss}), while the MR-CI results were obtained after singlet-triplet averaged calculations (CAS-SCF_{av} and MR-CI_{av}).

In Figure 1, some of the CAS-SCF valence orbitals are shown, for a chain of intermediate length (Be₇) at the equilibrium geometry. (The seven doubly occupied core orbitals (four σ_g and three σ_u) have been omitted). The six doubly occupied canonical orbitals (Figure 1a) are different bonding combinations of Be–Be *sp* hybrid orbitals. The two active natural orbitals (Figure 1b) are the singly occupied edge orbitals. They are hybrid *sp_z* orbitals pointing toward the outer part of the chain. In Table 1, for this same system, the orbital energies and the occupation numbers of the valence doubly occupied or active orbitals are reported. The singly occupied orbitals have negative energies, although much higher than the energies of the occupied orbitals. Their occupation numbers are very close to 1.0, the $8\sigma_g$ orbital being slightly more occupied than the $7\sigma_u$ one. This is not surprising, if one considers the fact that they correspond to the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), respectively. This confirms once more that these systems, at equilibrium, are biradicals whose electronic structure is very much reminiscent of the structure of an almost dissociated hydrogen molecule.

4.1. Optimized Geometries. In Table 2, the optimized bond lengths are reported. It appears that they depend in a very weak way on the bond position in the chain or the number of atoms in the chain. The general trends in bond lengths are more evident if one looks at Figure 2, where each curve is associated with a chain having a given value of *N* (*N* = 2 and *N* = 3 have been omitted). The external bond (labeled *N* – 2 in the figure) has a value of about 4.100 bohr. For all the chains, this is the longest one. This fact can be explained by the fact that the two terminal beryllium atoms are surrounded by only three electrons (instead of four, like all the remaining atoms placed in the inner region of the chain). The following bond (*N* – 4) is the shortest one for chains up to *N* = 8, and it is about 4.100 bohr. Then the bond lengths increase and saturate to a value close to 4.115 bohr. As a final remark, one can notice that the corresponding bond lengths in chains having different values of *N* are slightly shorter for the shortest chains.

4.2. Harmonic Frequencies. We computed numerical harmonic frequencies at the CAS-SCF(2/2) level, for both singlet and triplet states. It turns out that singlet and triplet have extremely close frequencies in the case of long chains,

since these two states are almost degenerated. In other words, this means that the singlet–triplet quasi degeneracy is not removed by small bendings (or stretchings) of the system. For this reason, we report in this work only the frequencies for the singlet states. Harmonic vibrational frequencies for the triplet and the singlet states are reported in the Supporting Information, while a graphical representation of the frequencies is illustrated in Figure 3a (stretching modes) and 3b (bendings). The lowest-mode frequencies, both for bending and stretching, go to zero for large values of *N*, while the highest frequencies tend to finite values. As a general rule, stretchings are associated with higher frequencies than bendings, as the stretching of bond lengths is more energetic than the bending of bond angles. In particular, the high-frequency limit for the stretchings is almost exactly twice as much as the corresponding value for the bendings. It is interesting to notice that the lowest modes for stretchings and bendings follow the trends expected for a classical flexible rod in the harmonic approximation. In fact, the lowest longitudinal and transversal modes for such a system are approximatively given by

$$\omega_{\text{long}}(k, L) = \alpha_{\text{long}} k/L \quad (1)$$

and

$$\omega_{\text{tran}}(k, L) = \alpha_{\text{tran}} (2k + 1)^2/L^2 \quad (2)$$

respectively (see, for instance, refs 23 and 24). In eqs 1 and 2 *L* is the length of the rod, *k* is a positive integer, while α_{long} and α_{tran} are constants depending on the material and the shape of the rod. Therefore, the lowest stretching modes are inversely proportional to the rod length, while the lowest bending modes are inversely proportional to the square of the length. In Figure 4a,b, we have reported the frequencies of the stretching and bending modes divided by *N* and *N*², respectively. It appears that the lowest curves are essentially constants and follow in a remarkable way eqs 1 and 2. As expected, the accord worsens as the frequency increases, and it is completely lost in the case of the highest modes.

4.3. Energies and Singlet–Triplet Splitting. In Table 3, the total energies, obtained through the different methods, are reported. The nature of the interaction between the two localized edge orbitals depends on the value of the Heisenberg coupling *J*. This is defined as the difference between

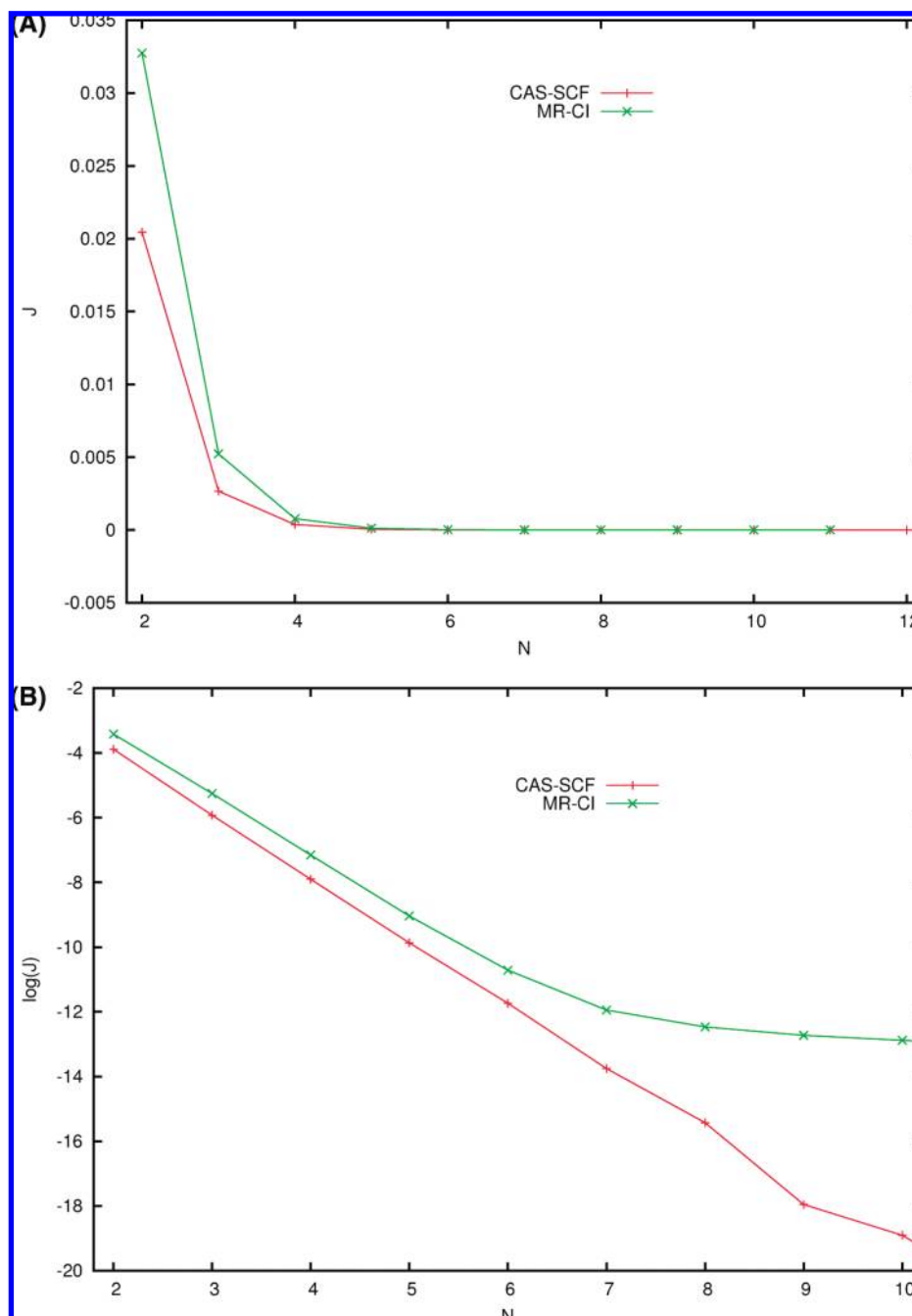


Figure 5. Singlet–triplet energy splitting (in hartree), $\Delta_{ST} = E_T - E_S$, as a function of N (a). Logarithm of the splitting (b). Red curves, CAS-SCF values; green curves, MR-CI values.

the triplet and the singlet energies. With this convention, a positive value of J corresponds to an antiferromagnetic coupling, as it happens for the chains we are discussing. A negative value of J , on the other hand, corresponds to a ferromagnetic coupling. The CAS-SCF and MR-CI splittings are shown in Figure 5a. It appears that the introduction of the dynamical correlation increases the value of the splitting by more than one-half with respect to the corresponding CAS-SCF values. In the region of small values of N , the CAS-SCF splitting goes exponentially to zero, as the number of beryllium atoms in the chain is increased, as shown in Figure 5b. In a logarithmic scale, the figure shows a linear behavior of J , both for CAS-SCF and MR-CI. The behavior of both MR-CI and CAS-SCF is linear up to $N = 6$, and the

two curves are parallel up to this value of N . For long chains ($N > 9$), the CAS-SCF split become unstable, being smaller than 10^{-8} hartree. The steep decrease of the (anti)ferromagnetic coupling with the distance of the center was already observed in other quasi-linear systems see for instance ref 25. It can be noticed from the logarithmic plot that the MR-CI split goes toward a constant value for chains longer than about ten atoms. This effect is most probably an artifact, and it could be due to the lack of size-consistency of the CI method. In fact, the energy split is severely underestimated at the CAS-SCF and MR-CI levels with respect to the FCI values,¹² while splits computed at a size-consistent level (NEVPT, see ref 26) do not present this behavior.²⁷

5. Conclusions

We presented a theoretical CAS-SCF study on the equilibrium geometry and harmonic frequencies of the so far hypothetical Be_N linear chains. According to our results, beryllium linear chains composed of *N* atoms are local minima on the corresponding PESs. Although the effect of dynamical correlation was not included in the study, we think unlikely that this could qualitatively change this conclusion. For this reason, linear Be_N systems could be metastable clusters.

The equilibrium bond distances of the clusters depend in a very weak way on the number of atoms or the position of the bond in the chain. The harmonic frequencies follow the trends expected for the corresponding vibration of a classical bar. Our calculation were performed by using a harmonic approximation, so no values were obtained for the higher coefficients. However, the fact that analytical and numerical approaches gave virtually identical results is an indicator that anharmonic effects could be relatively small.

The singlet–triplet energy splitting can be described by an antiferromagnetic Heisenberg phenomenological Hamiltonian. The magnetic coupling follows an exponentially decreasing pattern as a function of *N*, which is roughly proportional to the distance between the unpaired edge electrons. The importance of the introduction of dynamical correlation for a correct description of the splitting was confirmed: For a fixed value of *N*, the CAS-SCF value of *J* is about two-thirds of the corresponding MR-CI result.

Although the linear forms are predicted to be local minima on the PESs, more compact clusters have quite lower energies. The possible existence of these clusters in linear geometries depends on the barrier height toward more stable arrangements. Linear chains could be formed by depositing Be atoms on an inert surface. Another possibility could be the stabilization through an interaction of a beryllium chain with some other species. In this contest, the possibility of hosting these chains within nanotubes is particularly attractive. Therefore, in our opinion, it is worth investigating under what circumstances (if any) these linear structures could be stable.

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Supporting Information Available: Numerical values of computed harmonic frequencies for the various chains. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Emberly, E. G.; Kirczenow, G. *Phys. Rev. B* **1999**, *60*, 6028–6033.
- (2) Bahn, S. R.; Jacobsen, K. W. *Phys. Rev. Lett.* **2001**, *87*, 266101.
- (3) Himpsel, F. J.; Altmann, K. N.; Bennewitz, R.; Crain, J. N.; Kirakosian, A.; Lin, J.-L.; McChesney, J. L. *J. Phys.: Condens. Matter* **2001**, *13*, 11097–11113.
- (4) Amorim, E. P.; da Silva, A. J. R.; Fazzio, A.; da Silva, E. Z. *Nanotechnology* **2007**, *18*, 145701/1–4.
- (5) Crain, J. N.; Pierce, D. T. *Science* **2005**, *307*, 703.
- (6) Davidson, S. G.; Stšlicka, M. In *Basic Theory of Surface States*; Clarendon: Oxford, 1992.
- (7) Hod, O.; Peralta, J. E.; Scuseria, G. E. *Phys. Rev. B* **2007**, *76*, 233401.
- (8) Hod, O.; Barone, V.; Scuseria, G. E. *Phys. Rev. B* **2008**, *77*, 035411.
- (9) Soon, Y.-W.; Cohen, M. L.; Louie, S. G. *Nature (London)* **2006**, *444*, 347.
- (10) Monari, A.; Bendazzoli, G. L.; Evangelisti, S. *J. Chem. Phys.* **2008**, *129*, 134104.
- (11) Monari, A.; Vetere, V.; Bendazzoli, G. L.; Evangelisti, S.; Paulus, B. *Chem. Phys. Lett.* **2008**, *465*, 102–105.
- (12) Vetere, V.; Monari, A.; Scemama, A.; Bendazzoli, G. L.; Evangelisti, S. *J. Chem. Phys.* **2009**, *130*, 024301/1–9.
- (13) Salomonson, S.; Warston, H.; Lindgren, I. *Phys. Rev. Lett.* **1996**, *76*, 3092.
- (14) Tague, T. J.; Andrews, L. *J. Am. Chem. Soc.* **1993**, *115*, 12111–12116.
- (15) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.
- (16) MOLPRO is a package of ab initio programs written by the following: Werner, H.-J.; Knowles, P. J., with contribution from Almlöf, J., Amos, R. D., Berning, A., Deegan, M. J. O., Eckert, F., Elbert, S. T., Hampel, C., Lindh, R., Meyer, W., Nicklass, A., Peterson, K., Pitzer, R., Stone, A. J., Taylor, P. R., Mura, M. E., Pulay, P., Schütz, M., Stoll, H., Thorsteinsson, T., Cooper, D. L. (accessed March 10, 2009).
- (17) DALTON, a molecular electronic structure program, Release 2.0 (2005) see: <http://www.kjemi.uio.no/software/dalton/dalton.html> (accessed March 10, 2009).
- (18) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.
- (19) Knowles, P. J.; Werner, H.-J. *J. Chem. Phys.* **1985**, *82*, 5053.
- (20) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259.
- (21) Knowles, P. J.; Werner, H.-J. *J. Chem. Phys.* **1988**, *89*, 5803.
- (22) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.
- (23) Landau, L.; Lifschitz, E. In *Course Of Theoretical Physics*, 2nd ed.; Pergamon: Vol 7: Theory Of Elasticity, p 116.
- (24) Moloney, M. J. A. *J. Phys.* **2005**, *73*, 439–441.
- (25) Peng, S.-M.; Wang, C.-C.; Jang, Y.-L.; Chen, Y.-H.; Lin, F.-Y.; Mou, C.-Y.; Leung, M.-K. *J. Magn. Magn. Mater.* **2000**, *209*, 80–83.
- (26) Angeli, C.; Pastore, M.; Cimiraglia, R. *Theor. Chem. Acc.* **2007**, *117*, 743–754.
- (27) Pastore, M.; Monari, A.; Bendazzoli, G. L.; Cimiraglia, R.; Evangelisti, S. submitted to *J. Chem. Phys.*