

# Full configuration interaction calculation of singlet excited states of Be<sub>3</sub>

José Miguel Junquera-Hernández and José Sánchez-Marín<sup>a)</sup>

*Department de Química Física, Facultat de Químiques, Institut de Ciència Molecular, Universitat de València, Dr. Moliner, 50, E-46100 Burjassot (Valencia), Spain*

Gian Luigi Bendazzoli

*Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy*

Stefano Evangelisti

*Laboratoire de Physique Quantique, UMR 5626, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France*

(Received 28 June 2004; accepted 21 July 2004)

The full configuration interaction (FCI) study of the singlets vertical spectrum of the neutral beryllium trimer has been performed using atomic natural orbitals [ $3s2p1d$ ] basis set. The FCI triangular equilibrium structure of the ground state has been used to calculate the FCI vertical excitation energies up to 4.8 eV. The FCI vertical ionization potential for the same geometry and basis set amounts to 7.6292 eV. The FCI dipole and quadrupole transition moments from the ground state are reported as well. The FCI electric quadrupole moment of the  $X^3A'_1$  ground state has been also calculated with the same basis set ( $\Theta_{zz} = -2.6461$  a.u.,  $\Theta_{xx} = \Theta_{yy} = -1/2\Theta_{zz}$ ). Twelve of the 19 calculated excited singlets are doubly excited states. Most of the states have large multiconfigurational character. These results provide benchmark values for electronic correlation multireference methods. ( $4e \times 6MO$ )CAS-SDCI values for the same energies and properties are also reported. © 2004 American Institute of Physics. [DOI: 10.1063/1.1792152]

## I. INTRODUCTION

The search for highly accurate methods for the calculation of electronic excitation energies that can be successfully applied in very multiconfigurational situations is a permanent challenge for the researchers.<sup>1,2</sup> Quasidegenerated states having different physical nature, excitation energies of states dominated by diexcitations, and accurate descriptions of the bond breaking regions of excited state potential energy surfaces are some of the most difficult problems faced by high quality *ab initio* calculations. Most of these problems are usually treated by means of multireference configuration interaction approaches, more or less corrected for size-consistency error effects<sup>3-9</sup> or by multireference perturbation theory<sup>10-12</sup> approaches. The approaches based in the coupled-cluster (CC) ansatz, which so efficiently deal, the single reference level with the dynamic correlation effects, have now emerged as very promising methods that try to overcome the problem of a simultaneous and balanced treatment of nondynamic and dynamic correlation effects. Very hopeful developments have been recently reported in this most active field, and, in particular, some of them face the problem of the accurate calculation of excited states lead by diexcitations. Let us mention, just belonging to this last group, the completely renormalized equation-of-motion coupled-cluster approach with singles, doubles, and nonitera-

tive triples [CR-EOM-CCSD(T)],<sup>13</sup> the general-model-space state-universal coupled-cluster method (GMS SU CC),<sup>14,15</sup> the extended similarity transformed equation-of-motion coupled-cluster method (extended STEOM-CC),<sup>16</sup> or the equation-of-motion spin-flip coupled-cluster model with singles and doubles (EOM-SF-CCSD).<sup>17</sup> Many other multireference coupled-cluster approaches have been proposed in recent years to deal with multiconfigurational situations in either the ground state,<sup>18-20</sup> or the excited states (in most cases, both of them).<sup>21-23</sup> The so called nondynamical correlation energy has also received relevant attention in the framework of the CC theory, e.g., in the variationally optimized orbitals coupled-cluster of doubles approximation (VOO-CCD).<sup>24</sup> Multireference second order perturbation effects have also been added to this approach [VOO-CCD(2)]<sup>25</sup> and the relevance of approaches based in optimized orbitals for dealing with bond breaking has been tested against FCI benchmarks as well.<sup>26</sup> Other ways of dealing with electron correlation in the context of multireferential quantum chemical situations such as those based in the density matrix renormalization group have been proposed and favorably compared to FCI.<sup>27</sup>

The methods developed to calculate vertical excitation energies (VEE) can be conveniently tested against suitable benchmark calculations. In this way, the test can be performed directly without the need of calculating any other magnitude, and no ambiguity related to the experimental measurements is present (e.g., the exact occurrence of the 0-0 transition). The full configuration interaction (FCI)

<sup>a)</sup> Author to whom correspondence should be addressed; Fax: +34 96 354 3156. Electronic mail: jose.sanchez@uv.es

method provides the nonrelativistic exact eigenvalues and wave functions for a given one-particle basis set and provides a nonambiguous reference benchmark. Only a few systems have been calculated at the FCI level and only a limited number of their excited states show diexcited nature, so providing the required challenging target for the more sophisticated approached methods. With regard to singlet excited states dominated by diexcitations for which FCI results are available, we can mention the  $2^1\Sigma^+$ ,  $6^1\Sigma^+$ ,  $1^1\Delta$ ,  $2^1\Delta$ , and  $3^1\Pi$  states of  $\text{CH}^+$  cation,<sup>14,28,29</sup> the lowest energy  $^1\Delta_g$  and  $^1\Pi_g$  states of  $\text{C}_2$ ,<sup>30</sup> or the lowest  $^1\Delta$  state of  $\text{HB}$ .<sup>31</sup> Also for these systems, some excited states have important diexcitation contributions, such as the  $2^1\Pi$  state of  $\text{CH}^+$  (Refs. 28 and 29) and the lowest  $^1\Pi_u$  state of  $\text{N}_2$ .<sup>30</sup>

Beryllium atom is another system for which a diexcited state occurs at relatively low energies. The lowest singlet states manifold of Be atom has been calculated at the FCI level with a  $9s9p5d$  basis set by Koch and Harrison.<sup>32</sup> The diexcited  $(2p^2)^1D$  state was found at 7.0863 eV, just between the 6.7645 eV of the  $(2s3s)^1S$  and the 7.4597 eV of  $(2s3p)^1P^0$  single excited states. The  $(2p^2)^1D$  state occurs experimentally at 6.98 eV,<sup>33</sup> while the  $(2s3s)^1S$  occurs at 6.76 eV and the  $(2s3p)^1P^0$  occurs near 7.46 eV.<sup>33</sup> This fact is related to the availability of the empty  $2p$  valence orbitals in the formally valence closed shell  $1s^22s^2$  ground state of the atom. The  $2p$  orbitals make a decisive contribution to the chemical bond in  $\text{Be}_2$ <sup>34–38</sup> and one can expect from simple quantum mechanics arguments the occurrence of double excited states in Be clusters significantly below 7.0 eV.

The FCI ground state geometry of  $\text{Be}_3$  has been accurately determined for an ANOs  $[3s2p1d]$  basis set by the authors in a previous paper.<sup>39</sup> A preliminary CAS-SDCI calculation revealed that a significant number of multiconfigurational states, many of them of doubly excited nature, occur in the vertical spectrum of  $\text{Be}_3$  at excitation energies lesser than 5.0 eV. Hence, the first aim of the present paper is to provide FCI benchmark vertical excitation energies for the  $\text{Be}_3$  triatomic cluster. Moreover, FCI transition dipole moments and transition quadrupole moments (both of them in the property length approach) have been calculated, increasing in this way the very scarce FCI benchmark values available in the literature for these properties. It seems clear that the comparison of calculated electronic properties with those of reference calculations can provide additional tests on the quality of approximate wave functions. Unfortunately, the FCI benchmarks of dipole transition moment that one can find in the literature are still very scarce. We can mention the transitions from  $X^1\Sigma^+$  to three  $^1\Sigma^+$ , two  $^1\Pi$  and one  $^1\Delta$  states of  $\text{CH}^+$  (Ref. 28) and the  $X^1\Sigma_g^+ \rightarrow A^1\Pi_u$  transition of  $\text{C}_2$  (Ref. 40) as some of the very few ones for which FCI dipole transition moments have been reported. Also very scarce are the FCI reported values of ground state quadrupole moments (e.g., for BH and HF (Ref. 41)). Hence, a second aim of the present work is to provide a large set of FCI transition dipole and transition quadrupole moments. The electric quadrupole moment of the ground state is also reported as a benchmark reference.

## II. COMPUTATIONAL DETAILS

For the present calculation, the ANO basis set optimized by Widmark, Malmqvist, and Roos<sup>42</sup> was used, adopting the  $[3s2p1d]$  contraction from a  $14s9p4d$  primitive set. The equilibrium geometry of  $\text{Be}_3$  is that of a triangular  $D_{3h}$  molecule. All the calculations have been performed under the  $C_{2v}$  symmetry subgroup. The Be atoms have been placed at the points (0,1.312 998,0), (1.137 090,−0.656 499,0) and (−1.137 090,−0.656 499,0), with all distances in angstrom. This geometry is close to the actual FCI minimum within the uncertainty of the numerical round off. The self-consistent-field (SCF) energy is −43.714 915 883 4 a.u. No post-SCF adaptation of the molecular orbitals (MO) has been carried out, but the three lowest MOs, which combine mainly the three  $1s$  orbitals of atomic beryllium, were kept frozen after the SCF step. Hence, the FCI calculation involved 39 MOs and six active electrons. The orbital symmetry sets used in the FCI calculation in the  $C_{2v}$  group (triangular molecule) are  $15a_1$ ,  $7b_1$ ,  $12b_2$ ,  $5a_2$ , while the occupation set is  $2a_1$ ,  $1b_2$  that corresponds to the  $2a'_1$  and the  $2e'$  MOs of the  $D_{3h}$  group. The  $D_{3h}$  symmetry species resolve into the following  $C_{2v}$  symmetry species:  $A'_1 \rightarrow A_1$ ,  $A''_1 \rightarrow A_2$ ,  $A'_2 \rightarrow B_2$ ,  $A''_2 \rightarrow B_1$ ,  $E' \rightarrow A_1 + B_2$ , and  $E'' \rightarrow A_2 + B_1$ . Independent calculations have been performed at each of the four  $C_{2v}$  symmetries, even though low lying degenerated states were expected to be calculated twice as they behave as accidentally degenerated in  $C_{2v}$ . This was helpful in the assessment of symmetry assignments of the calculated states. It was also helpful in a few cases in which some states converged more easily in a particular  $C_{2v}$  symmetry representation.

The dimensions of the FCI matrices for  $a_1$ ,  $b_1$ ,  $b_2$ , and  $a_2$  representations were 20 900 733, 20 862 740, 20 897 740, and 20 860 108 Slater determinants, respectively.

The SCF calculations and bielectronic integrals transformation have been performed with the MOLCAS<sup>43</sup> code. The FCI calculations of energy and electrical properties have been performed with the VEGA code developed by some of us.<sup>44,45</sup> The VEGA program was adapted to the appropriate interfaces with MOLCAS.<sup>46</sup> A new interface program was written to convert MOLCAS property integrals file to a format readable by the VEGA program.

In all calculations 0.529 172 08 Å for Bohr radius and 27.211 40 eV for hartree have been used.

As it is explained above, a previous CAS-SDCI calculation was performed on the  $\text{Be}_3$  system with the same basis set. A small active space of four electrons on six molecular orbitals (MO) was employed. This space included the  $2e'$  occupied MO's and  $3a'_1$ ,  $3e'$ , and  $1a''_2$  virtual MOs. In some cases the FCI states, especially those having higher energies, were difficult to assign due to convergence issues. In these cases, the comparison of energies and properties of the FCI states with the CAS-SDCI ones was of great help in order to assess the assignment of the FCI states.

As concerns the FCI dipole and quadrupole matrix elements, the computation is performed as a scalar product in FCI space between the representative vector of the excited state  $|exc\rangle$  and that of  $|\mu|0\rangle$ , where  $\mu$  is the required component of the dipole or quadrupole operator and  $|0\rangle$  the ground

state eigenvector. As concerns the CAS-SDCI dipole and quadrupole moments matrix elements, the elements of  $\mu$  and  $\rho$  (the one-electron density matrix) are separately computed in the molecular spin-orbitals space before summing up the  $\mu_{ij}\rho_{ji}$  products.

### III. RESULTS

#### A. Vertical excitation energies

The FCI energies of the singlet states at the geometry of the ground state are reported in Table I. The FCI energy of the Be<sub>3</sub><sup>+</sup> cation resulting from the  $(2e')^{-1}$  ionization has been calculated with the same geometry and basis set as that used for the neutral molecule. The energy value is  $-43.601\,961\,630$  a.u., which results in a FCI vertical ionization potential of 7.6292 eV. Note that the vertical  $(2e')^{-1}$  ionization of Be<sub>3</sub> leads to a twofold degenerated  ${}^2E'$  state which in fact lies at the crossing of two Jahn-Teller symmetry-relaxed states. The vertical excitation energies of Be<sub>3</sub> in eV are reported also in Table I, as well as the dominant excitations in the wave function, for each state. The squares of all the determinant coefficients corresponding to any given  $n$ -electron excitation [described, e.g., as  $(2e')^{-2} \rightarrow (3a'_1)^{+2}$ , where  $n=2$ ], have been added up, including all the spin partners. The resulting weights are reported as percent contributions. Only those contributions having weights greater than 1% are reported in Table I. The 19 first converged singlet excited states are listed. All of them can be described, in the simplest way, as transitions from the  $2e'$  HOMO, but only seven of them, namely,  $1\,{}^1E''$ ,  $(1,5,6)\,{}^1E'$ ,  $1\,{}^1A'_2$ ,  $2\,{}^1A'_1$ , and  $3\,{}^1A'_1$ , have a single excitation as the leading term and can be properly described as single-excited states. All the others states have doubly excited character. In particular, the wave function for the second excited singlet, the  $1\,{}^1A''_1$  state, is lead by the open shell  $(2e'')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$  determinants, but it lies at 1.78 eV above the ground state and only 0.11 eV on top of the lowest excited singlet, the single-excited  $1\,{}^1E''(2e')^{-1} \rightarrow (1a''_2)^{+1}$  state. As a consequence of the twofold degenerated nature of the HOMO, both closed shell and open shell diexcited states have been found among the 12 diexcited states described in Table I. Closed shell diexcited states result when the holes in the leading diexcitations are originated in the same component of the degenerated  $2e'$  MO. This happens, e.g., in the first closed shell diexcited state (the  $3\,{}^1E'$  one) found at 3.08 eV. Other states dominated by closed shell diexcitations are  $4\,{}^1E'$  and  $3\,{}^1A'_1$ . The rest of diexcited states originate a hole in each component of the  $2e'$  MO, so that at least two unpaired electrons are required to describe the leading excitations. More commonly, four unpaired electrons are required in these cases, as it happens, e.g., in the lowest diexcited state, the  $1\,{}^1A''_1$ .

The multiconfigurational nature of most of the states in the Be<sub>3</sub> singlets manifold is clear from Table I. Let us point out some relevant facts, anyway. Only five of the states have a unique contribution greater than 1%. Noteworthy, only one of these is a single-excited state, the lowest singlet,  $1\,{}^1E''$ . Nine of the states have a dominant contribution weight lower than 50%. Four others have leading contributions between

50% and 60%. One of the states, the  $2\,{}^1A''_2$  state found at 4.12 eV, is dominated by two double excitations and a triple excitation involving four open shells (4.6%). Triple excitations are also relevant in two other states ( $4\,{}^1E''$  and  $5\,{}^1E''$ ). Quadruple excitations having a weight greater than 1% occur in the doubly excited state  $3\,{}^1A'_1$ .

The CAS(4×6)-SDCI vertical excitation energies are reported in Table II. The wave function contributions are not reported for simplicity, but the general overview of the states is similar to that of the FCI results reported in Table I. Only two states, namely, the  $3\,{}^1A'_1$  and  $5\,{}^1E''$  ones, are out of the space spanned by the CAS and could not be found. It would not be difficult to select a larger CAS set including the  $2a'_1$  MO. However, the smaller size of the active space helps to get a more patent effect of the CI truncation error and its associated size-extensivity error, which are noticeable in spite of the limited size of the virtual space and the small number of correlated electrons (six). One can see, by comparing Tables I and II, that the errors in VEE are small in some states (e.g., 0.4 mHartree for the  $1\,{}^1E'$ ) while the largest one amounts to about 7 mHartree (for the  $3\,{}^1A'_1$  state). As we will see below, the errors in the properties are distinctly larger.

#### B. Dipole and quadrupole transition moments

The FCI dipole and quadrupole transition moments between the GS and the excited singlets are reported in Table III. All the values are given in atomic units. Three significant decimal places are reported, but it must be noticed that the energies have been converged in most excited states up to six decimal places, and in the higher states, to five. The corresponding values for the CAS-SDCI calculations are reported in Table IV. Only the low lying diexcited states  $2\,{}^1E''$  and  $2\,{}^1E'$  show calculated transition moments nearly zero. However, the rest of the  ${}^1E'$  states (of which, the three, four, and five states are diexcited ones) show large dipole and quadrupole transition moment components. The largest transition dipole moments correspond to the very multiconfigurational  $5\,{}^1E'$  (diexcited) and  $6\,{}^1E'$  (single-excited) states. These are the highest calculated states, so that their oscillator strengths are the largest ones and transitions to them appear as the most allowed of the calculated ones.

The CAS-SDCI table of transition moments shows a general view similar to that of the FCI calculations, but both underestimation and overestimation occurs at the different values. Large differences between that values reported in Tables III and IV put forward a significant task for size-consistency correcting methods and for those approximated methods that accounts efficiently for high order perturbation effects. Most remarkable cases are the  $3\,{}^1E'$ ,  $5\,{}^1E'$ , and  $6\,{}^1E'$  excited states where the errors in the quadrupole transition moment components range from 0.4 to 0.7 a.u. It is noticeable that the largest error occurs in the  $3\,{}^1E'$  closed shell diexcited state, because it is not expected *a priori* that the chosen CAS is inappropriate for describing this mono-configurational state, as it can be the case for the  $5\,{}^1E'$  and  $6\,{}^1E'$  states.

TABLE I. Be<sub>3</sub> cluster. FCI [3s2p1d] energies and wave functions for singlet states up to 4.8 eV. See text for details.

State	FCI Energy (a.u.)	$\Delta E$ (eV) <sup>a</sup>	%	Contribution
$X^1A'_1$	-43.882 329 984		69.6	0⟩
			2.4	$(2e')^{-2} \rightarrow (3a'_1)^{-2}$
$1^1E''$	-43.820 924 8	1.67	65.7	$(2e')^{-1} \rightarrow (1a''_2)^{+1}$
$1^1A''_1$	-43.816 867	1.78	74.1	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$
$1^1E'$	-43.807 523 8	2.04	51.4	$(2e')^{-1} \rightarrow (3a'_1)^{-1}$
			7.2	$(2e')^{-2} \rightarrow (3a'_1)^{+2}$
			5.2	$(2e')^{-1} \rightarrow (3e')^{+1}$
			1.5	$(2e')^{-2} \rightarrow (3e')^{+2}$
$2^1E'$	-43.786 445	2.61	75.6	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
$2^1E'$	-43.783 74	2.68	78.0	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(3e')^{+1}$
$1^1A''_2$	-43.775 971 6	2.89	64.1	$(2e')^{-1} \rightarrow (3e')^{+1}$
			9.6	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(3e')^{+1}$
$2^1A'_1$	-43.775 256 1	2.91	48.7	$(2e')^{-1} \rightarrow (3e')^{+1}$
			9.5	$(2e')^{-2} \rightarrow (3a'_1)^{+2}$
			5.3	0⟩
			4.1	$(2a'_1)^{-1} \rightarrow (3a'_1)^{+1}$
$3^1E''$	-43.770 453 46	3.04	52.9	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$
			4.6	$(2e')^{-1} \rightarrow (1e'')^{+1}$
			4.2	$(2e')^{-1} \rightarrow (1a''_2)^{+1}$
			2.5	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
$3^1E'$	-43.769 046	3.08	63.6	$(2e')^{-2} \rightarrow (1a''_2)^{+2}$
$1^1A''_2$	-43.766 343 0	3.16	24.4	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$
			23.9	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
			12.3	$(2e')^{-1} \rightarrow (1e'')^{+1}$
			9.3	$(2a'_1)^{-1} \rightarrow (1a''_2)^{+1}$
$2^1A'_1$	-43.760 696	3.31	38.0	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$
			24.2	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
			4.2	$(2e')^{-1} \rightarrow (1e'')^{+1}$
$4^1E'$	-43.754 568 7	3.48	37.7	$(2e')^{-2} \rightarrow (3a'_1)^{+2}$
			10.4	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(3e')^{+1}$
			9.1	$(2e')^{-2} \rightarrow (3e')^{+2}$
			8.7	$(2e')^{-1} \rightarrow (3a'_1)^{+1}$
$3^1A'_1$	-43.748 68	3.64	57.5	$(2e')^{-2} \rightarrow (1a''_2)^{+2}$
			3.7	$(2e')^{-4} \rightarrow (3e')^{+2}(1a''_2)^{+2}$
			2.4	$(2a'_1)^{-2} \rightarrow (1a''_2)^{+2}$
			1.9	$(2e')^{-4} \rightarrow (3a'_1)^{+2}(1a''_2)^{+2}$
$4^1E''$	-43.738 828	3.90	59.8	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
			3.7	$(2e')^{-3} \rightarrow (3a'_1)^{+2}(1a''_2)^{+1}$
$3^1A'_1$	-43.735 87	3.99	41.6	$(2e')^{-1} \rightarrow (1e'')^{+1}$
			17.9	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$
$2^1A''_2$	-43.730 984 3	4.12	31.4	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}$
			23.6	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
			4.6	$(2e')^{-3} \rightarrow (3a'_1)^{+1}(1a''_2)^{+1}(3e')^{+1}$
$5^1E''$	-43.725 72	4.26	35.8	$(2e')^{-1} \rightarrow (1e'')^{+1}$
			22.5	$(2e')^{-2} \rightarrow (3e')^{+1}(1a''_2)^{+1}$
			4.4	$(2e')^{-3} \rightarrow (3a'_1)^{+2}(1a''_2)^{+1}$
$5^1E'$	-43.715 11	4.55	14.4	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(3e')^{+1}$
			11.7	$(2e')^{-2} \rightarrow (3e')^{+2}$
			9.8	$(2e')^{-1} \rightarrow (3e')^{+1}$
			6.7	$(2e')^{-1} \rightarrow (1a''_2)^{+1}$
			5.7	$(2a'_1)^{-1} \rightarrow (3e')^{+1}$
			3.5	$(2e')^{-1} \rightarrow (3a'_1)^{+1}$
$6^1E'$	-43.706 61	4.78	29.3	$(2e')^{-1} \rightarrow (3e')^{+1}$
			15.3	$(2e')^{-2} \rightarrow (3a'_1)^{+1}(3e')^{+1}$
			6.7	$(2e')^{-2} \rightarrow (3e')^{+2}$
			3.5	$(2e')^{-1} \rightarrow (3a'_1)^{+1}$
			3.0	$(2e')^{-1} \rightarrow (1a''_2)^{+1}$
			2.7	$(2a'_1)^{-1} \rightarrow (3e')^{+1}$

<sup>a</sup>The vertical FCI ionization potential is 7.629 eV. See text for further details.

All the components of the transition quadrupole moments have been included in Tables III and IV. Symmetry forces some of these components to have the same absolute value. However, they have been actually calculated indepen-

dently in the  $C_{2v}$  symmetry group, so that, in most cases, different components were calculated in completely independent runs. The only exceptions are the  $5^1E'$  and  $6^1E'$  states. For these states, only one FCI component was actually

TABLE II. Be<sub>3</sub> cluster. ( $4e \times 6MO$ )CAS-SDCI[ $3s2p1d$ ] energies for singlet states up to 4.9 eV.

State	$E$ (a.u.)	$\Delta E$ (eV)
X $^1A'_1$	-43 876 086	0,00
1 $^1E''$	-43 812 360	1,73
1 $^1A''_1$	-43 809 797	1,80
1 $^1E'$	-43 800 572	2,05
2 $^1E''$	-43 778 963	2,64
2 $^1E'$	-43 778 045	2,67
1 $^1A'_2$	-43 768 500	2,93
2 $^1A'_1$	-43 767 393	2,96
3 $^1E''$	-43 760 043	3,16
3 $^1E'$	-43 756 711	3,25
1 $^1A''_2$	-43 753 862	3,33
2 $^1A''_1$	-43 750 698	3,41
4 $^1E''$	-43 746 949	3,51
3 $^1A'_1$	-43 735 203	3,83
4 $^1E'$	-43 728 431	4,02
3 $^1A''_1$	Not found <sup>a</sup>	
2 $^1A''_2$	-43,719 379	4,26
5 $^1E''$	Not found <sup>a</sup>	
5 $^1E'$	-43 704 989	4,66
6 $^1E'$	-43 696 711	4,88

<sup>a</sup>The main contributions of the 3  $^1A''_1$  and 5  $^1E''$  states are not described by the selected CAS.

calculated because these states have not been reached in two independent symmetry calculations. The equality of the values helped us to state the accuracy of our calculations at the number of reported figures. So, for the 3  $^1A'_1$  state, the FCI quadrupole moment has been clearly determined with less accuracy than in the other states because the third decimal figure was not reproduced in independent (different symmetry) calculations.

### C. Molecular electric quadrupole moment for the ground state

As far as the authors know, only two studies that report FCI values for molecular electric quadrupole moments are

available in the literature. These are the BH and HF values calculated by Halkier *et al.*<sup>41</sup> employing large basis sets. We report here a FCI calculation of the molecular quadrupole moment for a nonlinear molecule. Both the FCI and the CAS-SDCI values for this property are reported in Table V. The energy for the ground state was converged at less than  $1 \times 10^{-8}$  a.u., so that the ground state property is given with four significant decimal places. The lack of at least a series of diffuse functions in the basis set makes these values of limited value if they were to be compared to measurements. However, they provide a benchmark reference for other calculations. Note, e.g., that the CAS-SDCI values are overestimated, as if one of the roles of the highest multiexcitations and of the highest order perturbation effects were to keep the electronic cloud a bit more tightly close to the origin. A similar behavior can be observed in the absolute values of the FCI and single-reference CC data of the traceless molecular electric quadrupole moment of BH and HF reported by Halkier, Larsen, and Olsen.<sup>41</sup> In order to make easier the comparisons with future calculations, we report both traced and traceless<sup>47,48</sup> electronic components as well as the total ones with the nuclei behaving as point charges. Let us note that having the center of mass as the origin of coordinates, the sum of the absolute values (in atomic units) of the diagonal components of the traced electronic quadrupole moments gives the expected value of  $r^2$  relative to that point. Hence,  $\langle r^2 \rangle$  amounts to 122.1495 a.u. for CAS-SDCI and to 120.2733 a.u. for FCI.

## IV. CONCLUSIONS

We have calculated FCI energies, transition moments, and wave functions description of the lower singlet excited states of the Be<sub>3</sub> molecule at its equilibrium geometry. Most of these states show doubly excited character. Some of these diexcited states have low VEE, and in particular, the first diexcited state appears at 1.78 eV. On the other hand, the

TABLE III. Be<sub>3</sub> cluster. FCI transition dipole and quadrupole moments (atomic units), and oscillator strengths. ... stands for symmetry forbidden. Signs are kept just for making clearer symmetry relationships among the different transition moment components.

State <sup>a</sup>	$ \mu $	$f$	$Q_{zz}$	$Q_{xx}$	$Q_{yy}$	$Q_{zz}=Q_{yz}$	$Q_{xy}$
1 $^1E''$	...	...	...	...	...	3.140	...
1 $^1E'$	0.721(x,y)	0.052	...	1.077	-1.077	...	1.077
2 $^1E''$	...	...	...	...	...	<0.001	...
2 $^1E'$	<0.001(x,y)	<0.001	...	<0.001	<0.001	...	<0.001
2 $^1A'_1$	...	...	0.171	-2.114	-2.114	...	...
3 $^1E''$	...	...	...	...	...	-1.546	...
3 $^1E'$	0.202(x,y)	0.006	...	1.067	-1.067	...	1.067
1 $^1A''_2$	0.615 (z)	0.029	...	...	...	...	...
4 $^1E'$	0.761(x,y)	0.097	...	-1.611	1.611	...	-1.611
3 $^1A'_1$	...	...	1.072	-0.862	-0.861	...	...
4 $^1E''$	...	...	...	...	...	0.337	...
2 $^1A''_2$	0.066 (z)	0.000	...	...	...	...	...
5 $^1E''$	...	...	...	...	...	1.662	...
5 $^1E'$	1.734(x,y)	0.671	...	0.570 <sup>b</sup>	-0.570 <sup>b</sup>	...	0.570
6 $^1E'$	2.063(x,y)	0.997	...	3.229 <sup>b</sup>	-3.229 <sup>b</sup>	...	3.229

<sup>a</sup> $A''_1$  and  $A'_2$  states are forbidden to  $\mu$  and  $Q$  transitions from the GS.

<sup>b</sup>Components that have not been actually obtained in separated calculation because these states were not reached in the  $A_1$  calculation with the  $C_{2v}$  symmetry.

TABLE IV. Be<sub>3</sub> cluster (4e×6MO)CAS-SDCI transition dipole and quadrupole moments (atomic units), and oscillator strengths. ... stands for symmetry forbidden. Signs are kept just for making clearer symmetry relationships among the different transition moment components.

State <sup>a</sup>	$ \mu $	$f$	$Q_{zz}$	$Q_{xx}$	$Q_{yy}$	$Q_{xz}=Q_{yz}$	$Q_{xy}$
1 <sup>1</sup> E''	...	...	...	...	...	3.223	...
1 <sup>1</sup> E'	0.719(x,y)	0.052	...	1.096	-1.096	...	1.096
2 <sup>1</sup> E''	...	...	...	...	...	<0.001	...
2 <sup>1</sup> E'	<0.001(x,y)	<0.001	...	<0.001	<0.001	...	<0.001
2 <sup>1</sup> A <sub>1</sub> '	...	...	0.155	-2.263	-2.263	...	...
3 <sup>1</sup> E''	...	...	...	...	...	-1.430	...
3 <sup>1</sup> E'	0.271(x,y)	0.012	...	1.747	-1.747	...	1.747
1 <sup>1</sup> A <sub>2</sub> ''	0.460 (z)	0.017	...	...	...	...	...
4 <sup>1</sup> E'	0.774(x,y)	0.103	...	-1.549	1.549	...	-1.549
3 <sup>1</sup> A <sub>1</sub> '	...	...	1.095	-0.700	-0.700	...	...
4 <sup>1</sup> E''	...	...	...	...	...	0.342	...
2 <sup>1</sup> A <sub>2</sub> ''	0.099 (z)	0.001	...	...	...	...	...
5 <sup>1</sup> E''	...	...	not found (not in CAS)				...
5 <sup>1</sup> E'	1.951(x,y)	0.869	...	1.154	-1.154	...	1.154
6 <sup>1</sup> E'	1.918(x,y)	0.880	...	2.851	-2.851	...	2.851

<sup>a</sup>A<sub>1</sub>'' and A<sub>2</sub>' states are forbidden to  $\mu$  and  $Q$  transitions from the GS.

nature of many of these states is highly multiconfigurational. Only a small number of states can be properly described by just one excitation.

We report also the results from a CAS-SDCI calculation of these excited states. The deviation of the results from FCI ones is more important in the calculated transition moments than in the energy of the states.

The calculated values of the dipole transition moment on non-symmetry-forbidden transitions are of significant value in all states but one. In addition, most of the dipole forbidden transitions from the GS involve states which show significant quadrupole transition moment and thus are quadrupole allowed. The calculated transition moments are not quantitatively comparable to experimental values, in the case that these would exist, due to the small size of the basis set. In spite of that, a qualitative picture of the spectrum can be attempted. The main expected feature below 5 eV should be a broad band around 4.5–4.8 eV originated by the transitions to 5 <sup>1</sup>E' and 6 <sup>1</sup>E' states that show the greatest transition dipole moment. We can expect also small bands around 3.1–3.5 eV and around 2.0 eV due to the 3 <sup>1</sup>E', 1 <sup>1</sup>A<sub>2</sub>'', and 4 <sup>1</sup>E' transitions on the one hand and to the 1 <sup>1</sup>E' transition on the other. Other bands, if observed, could be originated by the

quadrupole allowed transitions. The transition to the first excited singlet, 1 <sup>1</sup>E'' is dipole forbidden but shows a relatively large quadrupole transition moment.

The present work increases considerably the available FCI benchmark values of excitation energies to diexcited states and multiconfigurational excited states, and, most noticeably, those for dipole transition moments and quadrupole transition moments.

## ACKNOWLEDGMENTS

The authors wish to thank Dr. Daniel Maynau for his assistance in the adaptation of the VEGA code to work with other codes. This work has been supported by Spanish MCT (Plan Nacional I+D+I and European Funds, Project No. BQU2001-2935-C02-01), DGEUI (Generalitat Valenciana Projects No. INF01-051 and INFRA03-047) and EU COST action D-23. J.M.J.-H. acknowledges the Spanish MECED for a FPU grant.

TABLE V. FCI[3s2p1d] and CAS-SDCI quadrupole moment components of Be<sub>3</sub> ground state in atomic unit Nondiagonal components are null.

Method	$Q_{zz}$	$Q_{xx}=Q_{yy}$
Traced (electronic)		
CAS-SDCI	14.2005	53.9745
FCI	13.7015	53.2859
Traceless (electronic)		
CAS-SDCI	-39.7740	19.8870
FCI	-39.5844	19.7922
Traceless (total)		
CAS-SDCI	-2.8357	1.4178
FCI	-2.6461	1.3231

<sup>1</sup>Recent Advances in Coupled Cluster Methods, edited by R. J. Bartlett (World Scientific, Singapore, 1997).

<sup>2</sup>Recent Advances in Multireference Methods, edited by K. Hirao (World Scientific, Singapore, 1999).

<sup>3</sup>G. F. Bauerfeldt and H. Lischka, J. Phys. Chem. A **108**, 3111 (2004).

<sup>4</sup>D. P. Schofield and H. G. Kjaergaard, J. Chem. Phys. **120**, 6930 (2004).

<sup>5</sup>X. Z. Yang, M. R. Lin, and B. Z. Zhang, J. Chem. Phys. **120**, 7470 (2004).

<sup>6</sup>W. Eisfeld, J. Chem. Phys. **120**, 6056 (2004).

<sup>7</sup>J. Pitarch-Ruiz, S. Evangelisti, and D. Maynau, Int. J. Quantum Chem. **97**, 688 (2004).

<sup>8</sup>D. Walter, A. Venkatnathan, and E. A. Carter, J. Chem. Phys. **118**, 8127 (2003).

<sup>9</sup>A. I. Krylov, Chem. Phys. Lett. **350**, 522 (2001).

<sup>10</sup>H. A. Witek, H. Nakano, and K. Hirao, J. Chem. Phys. **118**, 8197 (2003).

<sup>11</sup>C. Angeli, S. Borini, and R. Cimraglia, Theor. Chem. Acc. **111**, 352 (2004).

<sup>12</sup>Y. G. Khait, J. Song, and M. R. Hoffmann, J. Chem. Phys. **117**, 4133 (2002).

<sup>13</sup>K. Kowalsky and P. Piecuch, J. Chem. Phys. **120**, 1715 (2004).

<sup>14</sup>X. Li and J. Paldus, J. Chem. Phys. **120**, 5890 (2004).

<sup>15</sup>X. Li and J. Paldus, J. Chem. Phys. **119**, 5320 (2003).

<sup>16</sup>M. Nooijen and V. Lotrich, J. Chem. Phys. **113**, 494 (2000).

<sup>17</sup>S. V. Levchenko and A. I. Krylov, J. Chem. Phys. **120**, 175 (2004).

- <sup>18</sup>I. S. O. Pimienta, K. Kowalski, and P. Piecuch, *J. Chem. Phys.* **119**, 2951 (2003).
- <sup>19</sup>S. Li, J. Ma, and Y. Jiang, *J. Chem. Phys.* **118**, 5736 (2003).
- <sup>20</sup>J. Pittner, *J. Chem. Phys.* **118**, 10876 (2003).
- <sup>21</sup>M. Kállay, P. G. Szalay, and P. R. Surján, *J. Chem. Phys.* **117**, 980 (2002).
- <sup>22</sup>L. Adamowicz, J. P. Malrieu, and V. V. Ivanov, *J. Chem. Phys.* **112**, 10075 (2000).
- <sup>23</sup>U. S. Mahapatra, B. Datta, and D. Mukherjee, *Mol. Phys.* **94**, 157 (1998); *J. Chem. Phys.* **110**, 6171 (1999).
- <sup>24</sup>A. I. Krylov, C. D. Sherrill, E. F. C. Byrd, and M. Head-Gordon, *J. Chem. Phys.* **109**, 10669 (1998).
- <sup>25</sup>S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, *J. Chem. Phys.* **113**, 3548 (2000).
- <sup>26</sup>A. Dutta and C. D. Sherrill, *J. Chem. Phys.* **118**, 1610 (2003).
- <sup>27</sup>G. K. Chan and M. Head-Gordon, *J. Chem. Phys.* **116**, 4462 (2002).
- <sup>28</sup>J. Olsen, A. M. Sánchez de Merás, H. J. Aa. Jensen, and P. Jorgensen, *Chem. Phys. Lett.* **154**, 380 (1989).
- <sup>29</sup>A. I. Krilov, C. D. Sherrill, and M. Head-Gordon, *J. Chem. Phys.* **113**, 6509 (2000).
- <sup>30</sup>O. Christiansen, H. Koch, P. Jorgensen, and J. Olsen, *Chem. Phys. Lett.* **256**, 185 (1996).
- <sup>31</sup>H. Koch, O. Christiansen, P. Jorgensen, and J. Olsen, *Chem. Phys. Lett.* **244**, 75 (1995).
- <sup>32</sup>H. Kock and R. J. Harrison, *J. Chem. Phys.* **95**, 7479 (1991).
- <sup>33</sup>C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1952).
- <sup>34</sup>R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.* **123**, 321 (1986).
- <sup>35</sup>J. D. Watts, I. Cernusak, J. Noga, R. J. Bartlett, C. W. Bauschlicher, Jr., T. J. Lee, A. P. Rendell, and P. R. Taylor, *J. Chem. Phys.* **93**, 8875 (1990).
- <sup>36</sup>L. Füsti-Molnár and P. G. Szalay, *Chem. Phys. Lett.* **258**, 400 (1996).
- <sup>37</sup>S. Evangelisti, G. L. Bendazzoli, R. Ansaloni, F. Duri, and E. Rosi, *ChemPhysChem* **252**, 437 (1996).
- <sup>38</sup>J. Noga, W. Kutzelnigg, and W. Klopper, *Chem. Phys. Lett.* **199**, 497 (1992).
- <sup>39</sup>J. M. Junquera-Hernández, J. Sánchez-Marín, G. L. Bendazzoli, and S. Evangelisti, *J. Chem. Phys.* **120**, 8405 (2004).
- <sup>40</sup>S. Langhoff, C. W. Bauschlicher, A. Rendell, and A. Komornicki, *J. Chem. Phys.* **92**, 3000 (1990).
- <sup>41</sup>A. Halkier, H. Larsen, J. Olsen, P. Jorgensen, and J. Gauss, *J. Chem. Phys.* **110**, 734 (1999).
- <sup>42</sup>P.-O. Widmark, P.-A. Malmqvist, and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
- <sup>43</sup>K. Andersson, M. Barysz, A. Bernhardsson *et al.*, MOLCAS, Version 5.4 (Lund University, Sweden, 2002).
- <sup>44</sup>G. L. Bendazzoli and S. Evangelisti, *J. Chem. Phys.* **98**, 3141 (1993).
- <sup>45</sup>G. L. Bendazzoli and S. Evangelisti, *Int. J. Quantum Chem., Symp.* **27**, 287 (1993).
- <sup>46</sup>D. Maynau, MOLCOST, Toulouse University, France (2003).
- <sup>47</sup>A. D. Buckingham, *J. Chem. Phys.* **30**, 1580 (1959).
- <sup>48</sup>A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).