

## Nondipole bound anions: $\text{Be}_2^-$ and $\text{Be}_3^-$

Ilya G. Kaplan<sup>a)</sup>

*Instituto de Investigaciones en Materiales, Universidad Autónoma de México, Apdo. Postal 70-360, 04510 México, D.F., México and Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701*

Olga Dolgounitcheva

*Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701*

John D. Watts

*Department of Chemistry, Jackson State University, Jackson, Mississippi 39217*

J. V. Ortiz

*Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701*

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Electron affinities (EAs) of beryllium clusters are calculated up to the complete coupled-cluster single double triple (CCSDT) level using reasonably large basis sets with many diffuse functions. At all levels of theory, the obtained values for the adiabatic EA are large enough to be observed with standard photodetachment techniques. The vertical electron detachment energy is 0.341 eV for  $\text{Be}_2^-$  and is 1.470 eV for  $\text{Be}_3^-$  at the most precise CCSDT level. All studied beryllium anions are valence bound but the nature of binding is different in  $\text{Be}_2^-$  and the two  $\text{Be}_3^-$  isomers. The only factor of stabilization of the excess electron in  $\text{Be}_2^-$  is the relaxation energy.  $\text{Be}_3^-(D_{\infty h})$  is stabilized by the relaxation energy and the Koopmans electrostatic and exchange energies; in  $\text{Be}_3^-(D_{3h})$ , the main factors of stabilization are the correlation and relaxation energies. As was revealed in our study, in linear molecules the correlation contribution to the electron binding energy is negative, i.e., it decreases the EA. © 2002 American Institute of Physics. [DOI: 10.1063/1.1494801]

### I. INTRODUCTION

In many molecular anion studies carried out in the last decade, the anions are considered to be dipole bound. The problem of dipole-bound molecular anions has a long history,<sup>1–20</sup> starting in 1947 with a seminal paper by Fermi and Teller<sup>1</sup> and extending to the present.<sup>19,20</sup> Fermi and Teller<sup>1</sup> considered the capture of a negative meson by a proton and formation of a  $\pi^- \text{H}^+$  atom. They have found that bound states exist only if the value of dipole moment,  $\mu$ , exceeds 1.625 D. The subsequent studies of more realistic models revealed that for the formation of anions with magnitudes of the electron binding energy,  $\Delta E_e$ , which can be measured,  $\mu_{\text{min}}$  must be larger than 2.5 D. This conclusion was confirmed in experiments by Desfrancois *et al.*<sup>10</sup> According to their data, the lowest molecular dipole moment associated with an experimentally observed anion was  $\mu = 2.66 \pm 0.06$  D.

The simplest way to estimate  $\Delta E_e$  is to find the energy of the relevant unfilled orbital in the Hartree–Fock (HF) method. According to the Koopmans theorem (KT),<sup>21</sup> the difference between the HF energy of a neutral molecule and the energy of an anion described by the HF orbitals of the neutral molecule is equal to the negative of the relevant orbital energy, which usually is  $-\epsilon_{\text{LUMO}}$ . The energy found in this approach,  $\Delta E_e^{\text{KT}}$ , does not include orbital relaxation and

electron correlation effects. In early studies of the electron binding energies of anions, the Koopmans approach was adopted.<sup>4,6–9</sup> Later, experimental data indicated that in many cases  $\Delta E_e^{\text{KT}}$  is considerably smaller than the measured values. This discrepancy motivated Gutowski *et al.*<sup>13–16</sup> to study the role of the electron correlation in the binding of an “extra” electron to polar molecules. They decomposed the electron correlation contribution at the MP2 level,  $\Delta E_e^{\text{MP2}}$ , into a dispersion part  $\Delta E_e^{\text{MP2-disp}}$  and the remainder  $\Delta E_e^{\text{MP2-no-disp}}$ . For all studied anions,<sup>16</sup> the contribution of the dispersion interactions has the same or a larger magnitude than  $\Delta E_e^{\text{KT}}$ . However, it is worth-while to note that the expression for the dispersion energy  $\Delta E_e^{\text{MP2-disp}}$  used in Refs. 13–16 is defined with relaxed HF orbitals of the anion, and therefore it contains relaxation effects. As stressed by the authors,<sup>14</sup>  $\Delta E_e^{\text{MP2-disp}}$  takes into account the proper permutation symmetry of all electrons in the anion; this quantity therefore contains exchange effects as well. Hence,  $\Delta E_e^{\text{MP2-disp}}$  is not purely dispersion energy and may considerably differ from the latter. The dispersion energy can be rigorously defined only at large distances where overlap between interacting subsystems is negligible.<sup>22</sup> In supermolecular studies of the nature of binding, it is more appropriate to apply the electron correlation concept.<sup>23,24</sup>

The total contribution of the electron correlation energy to the electron affinity (EA),  $\Delta E_e^{\text{corr}}$ , found at the coupled-cluster single double triple [CCSD(T)] level in Refs. 13–16, is larger than the  $\Delta E_e^{\text{KT}}$  contribution for most of the studied anions. For  $\text{C}_4^-\text{H}_2$  it is as much as three times larger. Thus,

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: kaplan@fisica.unam.mx

the general conclusion<sup>13,15,16</sup> about the importance of taking electron correlation corrections into account in the study of the binding of an extra electron to polar molecules is supported by computational data. However, in some anions the picture becomes different. The  $\Delta E_e^{\text{corr}}$  at the CCSD(T) level can be negative, i.e., electron correlation effects decrease the binding energy of attached electron in an anion. It takes place<sup>16</sup> in  $\text{HCN}^-$  where  $\Delta E_e^{\text{corr}} = -5.2 \text{ cm}^{-1}$  and in  $\text{CH}_3\text{F}^-$  where  $\Delta E_e^{\text{corr}} = -34 \text{ cm}^{-1}$ . These anions are stabilized by the electrostatic forces included in  $\Delta E_e^{\text{KT}}$ . As follows from the recent study by Gutowski and Skurski<sup>18</sup> of the linear anions  $(\text{HCN})_n^-$ , the contribution of  $\Delta E_e^{\text{KT}}$  is dominant for their stabilization. Relaxation effects contribute less than 10%, whereas electron correlation corrections at the MP2 level actually diminish the EA.

Nonpolar molecules with high symmetry repel an additional electron. Gutsev and Adamowicz<sup>11</sup> demonstrated that the  $\text{CF}_4$  molecule does not attach an electron in its ground state. The adiabatic electron affinity has been found to be clearly negative,  $-1.22 \text{ eV}$ . This molecule possesses the  $T_d$  point-group symmetry. From this it follows that the first nonvanishing multipole moment in  $\text{CF}_4$  is the octopole.<sup>22</sup> It is important to study anion formation in the case of nonpolar molecules with symmetry lower than  $T_d$ .

In this context, weakly bound clusters of alkaline-earth elements such as  $\text{Be}_n$  and  $\text{Mg}_n$  are interesting. The Be atom binds an additional electron only in the excited  $1s^2 2s 2p^3 \text{P}$  state. The experimental electron affinity,  $290.99 \pm 0.10 \text{ meV}$ ,<sup>25</sup> corresponds to the  $1s^2 2s 2p^2 \text{ } ^4\text{P}$  state of the  $\text{Be}^-$  anion. A theoretical calculation<sup>26</sup> predicted a rather close value of  $289.10 \text{ meV}$ . One may expect  $\text{Be}_n$  clusters to form stable anions in their ground states.

The first qualitative calculations of electron affinities of small  $\text{Be}_n^-$  anions ( $n=2-4$ ) were carried out by Jordan and Simons.<sup>27-29</sup> They predicted the anions to be stable with respect to the neutral  $\text{Be}_n$  clusters with rather large values of EA. For  $\text{Be}_2^-$  this conclusion was confirmed in more precise calculations by Bauschlicher and Partridge.<sup>30</sup> Most of the subsequent beryllium cluster calculations focus on neutral clusters<sup>31-35</sup> (see also Refs. 23, 24, and references therein). Special attention was paid to  $\text{Be}_2$ .<sup>36-39</sup> However, methods of such high precision are difficult to apply to larger clusters.

In this work we calculate the electron affinities of  $\text{Be}_2$  and  $\text{Be}_3$  at different levels of accuracy up to the CCSD(T) and CCSDT levels. These calculations use reasonably large basis sets with many diffuse functions. The decomposition of the binding energy of the attached electron into physical components and the comparative analysis of their contributions elucidate the nature of anion formation in the  $\text{Be}_2$  and  $\text{Be}_3$  clusters.

## II. ENERGY DECOMPOSITION FORMULAE AND COMPUTATIONAL DETAILS

In variational methods (as well as in the Møller–Plesset perturbation approach), the binding energy is defined as a difference between total energies. In the anion case, the binding energy of an attached electron (the electron affinity, EA) is equal to

$$\Delta E_e = EA = E_n(N) - E_a(N+1), \quad (1)$$

where  $N$  denotes a neutral molecule or cluster and  $N+1$  denotes an anion;  $n$  and  $a$  label the electronic states of neutral and charged systems, respectively. Depending on the inter-nuclear distances at which  $E(N)$  and  $E(N+1)$  are calculated, EA is classified as:

- Vertical electron affinity (VEA)—both energies in Eq. (1) are calculated at the equilibrium structure of the neutral system;
- Adiabatic electron affinity (AEA)—energies in Eq. (1) are calculated at the equilibrium structures of the neutral and charged systems, respectively; and
- Vertical electron detachment energy (VEDE)—energies in Eq. (1) are calculated at the equilibrium structure of the charged system.

Because of difficulties in the definition of the dispersion energy in anion systems mentioned in Sec. I, we will not decompose the correlation contribution into the dispersion and nondispersion parts. The energy decomposition used in our study is the following:

$$\Delta E_e = \Delta E_e^{\text{KT}} + \Delta E_{\text{relax}}^{\text{SCF}} + \Delta E_e^{\text{corr}}. \quad (2)$$

For the ground electronic state, Eq. (1) is written as

$$\Delta E_e = E_0(N) - E_0(N+1). \quad (1)$$

The Koopmans approach corresponds to the SCF method in which both energies in Eq. (1) are calculated with SCF orbitals of the neutral system

$$\Delta E_e^{\text{KT}} = E_0^{\text{SCF}}(N) - E_0^{\text{SCF}}(N+1)_{\text{nonrelax}}. \quad (3)$$

According to the Koopmans theorem<sup>21</sup>

$$\Delta E_e^{\text{KT}} = -\varepsilon_e, \quad (4)$$

where  $\varepsilon_e$  is the energy of the orbital occupied by the attached electron in an anion and corresponding to one of virtual orbitals of neutral system. Thus, the KT approximation does not take relaxation effects into account and includes only electrostatic and exchange interactions at the SCF level. The remainder of the binding energy at the SCF level we denote as the relaxation energy

$$\Delta E_{\text{relax}}^{\text{SCF}} = \Delta E_e^{\text{SCF}} - \Delta E_e^{\text{KT}}, \quad (5)$$

which stems from the relaxation of the orbitals of the neutral system in the field of the attached electron.  $\Delta E_{\text{relax}}^{\text{SCF}}$  consists mostly of the induction (polarization) energy, but contains also the exchange energy that cannot be separated.

The electron correlation contribution is defined as usual,<sup>35</sup> following the general definition of Löwdin:<sup>40</sup>

$$\Delta E_e^{\text{corr}} = \Delta E_e - \Delta E_e^{\text{SCF}} \quad (6)$$

and depends upon the correlation method used. If the CCSD(T) method is employed,

$$\Delta E_e^{\text{corr}}[\text{CCSD(T)}] = \Delta E_e^{\text{CCSD(T)}} - \Delta E_e^{\text{SCF}}. \quad (7)$$

TABLE I.  $\text{Be}_2$  and  $\text{Be}_2^-$ . Dependence of the ground state energy (atomic units) on the basis set.  $\text{Be}_2$  is calculated at the equilibrium distance of  $\text{Be}_2$ ; for the basis sets 1 and 2, Be–Be distance is equal to 2.528 Å, for 3 and 4 it is equal to 2.523 Å.

Species	Energy	Basis set			
		1	2	3	4
$\text{Be}_2 \ ^1\Sigma_g^+$	HF	–29.133 58	–29.133 59	–29.135 52	–29.135 52
	MP2	–29.201 30	–29.201 32	–29.205 14	–29.204 46
	MP4(SDTQ)	–29.229 32	–29.229 32	–29.232 41	–29.232 24
	CCSD(T)	–29.236 88	–29.236 89	–29.239 98	–29.239 79
$\text{Be}_2^- \ ^2\Sigma_g^+$	PUHF	–29.146 70	–29.146 77	–29.148 83	–29.148 76
	MP2	–29.217 62	–29.217 96	–29.221 89	–29.220 34
	MP4	–29.243 75	–29.244 17	–29.247 44	–29.246 16
	CCSD(T)	–29.248 50	–29.249 12	–29.252 32	–29.251 10

The expression for the electron correlation contribution to the EA, Eqs. (6) and (7), can be represented via the electron correlation contributions,  $\Delta E_{\text{corr}}$ , to the total energies of neutral and anionic cluster, namely,

$$\Delta E_E^{\text{corr}} = \Delta E_{\text{corr}}(N) - \Delta E_{\text{corr}}(N+1), \quad (8)$$

where

$$\Delta E_{\text{corr}} = E_0(\text{correlated}) - E_0^{\text{SCF}}. \quad (9)$$

The correlation contribution to a binding energy reduces to the dispersion energy at large distances where exchange effects are negligible, see calculations for  $\text{Be}_2$  and other alkaline-earth dimers.<sup>23</sup>

The present calculations were performed with the GAUSSIAN-99 development version suite of programs<sup>41</sup> and the ACES II program.<sup>42,43</sup> Figures were generated with the MOLDEN package.<sup>44</sup> Geometry optimizations of neutral and anionic species were performed at the CCSD(T) level<sup>45</sup> with the 6-311+ $G(3d2f)$  basis set.<sup>46–48</sup> For  $\text{Be}_2$  and  $\text{Be}_2^-$ , geometry optimizations were performed also at the complete CCSDT level<sup>49–51</sup> with the same basis set. Some CCSDT calculations were performed on  $\text{D}_{3h}\text{Be}_3$  and  $\text{Be}_3^-$  using the 6-311+ $G(3df)$  basis set. Unrestricted Hartree–Fock (UHF) reference functions were used in the calculations on the anions, and the spin contamination was monitored at the HF and CC levels. For  $\text{Be}_2^-$  the spin contamination was completely negligible. The spin contamination at the HF level for  $\text{D}_{3h}\text{Be}_3^-$  was significant ( $2S+1=2.7$ ), but at the CCSDT level it was minor ( $2S+1=2.02$ ). To eliminate the spin contamination in the MP calculations, the spin projection procedure,<sup>52</sup> embedded in the Gaussian suite, was employed.

Two structures were considered in the case of  $\text{Be}_3$ : an equilateral triangle ( $\text{D}_{3h}$  symmetry) and a linear structure ( $\text{D}_{\infty h}$  symmetry). The  $\text{D}_{3h}$  structure is considerably lower in energy, by 0.315 eV at the CCSD(T) level, and represents the global minimum. Efforts to obtain an anion with lower symmetry ( $\text{C}_{2v}$ ) led back to the  $\text{D}_{3h}$  structure.

The symmetry of the ground electronic state of  $\text{Be}_2^-$  is  $^2\Sigma_g^+$ . In case of linear  $\text{Be}_3^-$ , the ground electronic state of the anion is  $^2\Sigma_u^+$ . In the  $\text{D}_{3h}$  geometry,  $\text{Be}_3$  has two closely lying unoccupied MOs of  $a_1''$  and  $a_2''$  symmetries. As a result, two anions with different symmetry in the singly occupied MO (SOMO) can be formed, both possessing the  $\text{D}_{3h}$  point

symmetry. Here we considered the anion with lower energy,  $^2A_2''$ . It is an anion with  $1a_2''$  symmetry in the SOMO originating from the electron attachment to a lowest unoccupied molecular orbital (LUMO)+1 of  $\text{Be}_3$  ( $\text{D}_{3h}$ ).

It is well known that basis sets used for anion calculations have to contain diffuse functions with high angular momenta in addition to standard valence basis functions in order to describe the charge distribution of an attached electron. They also have to be flexible enough to describe large relaxation effects upon electron attachment. Although the 6-311+ $(3d2f)$  basis set provided by the Gaussian suite is rather flexible, nevertheless, it is worth-while to check it by comparison with some larger basis sets. In this connection, we studied several basis alternatives including the correlation consistent, aug-cc-pVQZ set.<sup>53,54</sup>

In Table I, the basis set dependence of the ground state energy of neutral and anionic beryllium dimer is presented for four basis sets: (1) 6-311+ $(3d2f)$ ; (2) 6-311+ $G(3d2f)$  augmented with extra  $s$  and  $p$  diffuse functions with an exponent equal to 0.33 of the standard diffuse Be exponents; (3) the aug-cc-pVQZ basis created for  $\text{Be}^{55}$  (extra diffuse functions were obtained in the same manner as earlier); (4) aug-cc-pVQZ with  $d$ ,  $f$ , and  $g$  diffuse functions dropped and extra  $s$  and  $p$  ones added with exponents obtained as described for basis set (2). As follows from these data, the aug-cc-pVQZ basis set gives values of the total energy that are lower than those of the other three. The energy values (in atomic units) differ in the third digit; the differences for the anion are larger than for the neutral dimer. The largest differences in total energies are between basis sets (3) and (1) at the CCSD(T) level,  $\Delta E_0(\text{Be}_2)_{3-1}=0.084$  eV and  $\Delta E_0(\text{Be}_2^-)_{3-1}=0.104$  eV. This means that for the VEA, the maximum difference does not exceed 0.02 eV or 6% of the VEA magnitude. Thus, the more convenient (in the frame of the Gaussian suite) 6-311+ $(3d2f)$  basis set can be employed with good accuracy.

### III. RESULTS AND DISCUSSION

Results obtained at different levels of theory are presented in Table II in the order of a more precise account of the electron correlation. For  $\text{Be}_2$ , the highest applied level was the complete CCSDT method,<sup>49–51</sup> for  $\text{Be}_3$  the highest

TABLE II. Total ground state energies (atomic units) and electron affinities (electron volts), calculated at different levels of theory with the 6-311+*G*(3*d2f*) basis set.

	KT	PUHF	MP2	MP3	MP4(SDTQ)	CCSD(T)	CCSDT
Be <sub>2</sub> <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> <i>a</i>		-29.133 58	-29.201 30	-29.220 10	-29.229 32	-29.236 88	-29.237 67
Be <sub>2</sub> <sup>-</sup> 2Σ <sub>g</sub> <sup>+</sup> <i>a</i>		-29.146 32	-29.217 84	-29.235 45	-29.243 95	-29.248 78	-29.250 05
VEA	-0.249	0.357	0.442	0.410	0.392	0.316	0.332
AEA		0.347	0.450	0.418	0.398	0.324	0.337
VEDE	-0.203	0.402	0.467	0.423	0.405	0.327	0.341
Be <sub>3</sub> <sup>1</sup> A <sub>1</sub> ' <i>b</i>		-43.714 93	-43.846 10	-43.867 23	-43.881 46	-43.886 98	
Be <sub>3</sub> <sup>-</sup> 2A <sub>2</sub> ' <i>b</i>		-43.740 74	-43.902 52	-43.918 78	-43.937 59	-43.939 72	
VEA	0.132	0.684	1.462	1.354	1.482	1.377	
AEA		0.702	1.535	1.402	1.527	1.435	
VEDE	0.133	0.754	1.589	1.469	1.599	1.488	

<sup>a</sup>CCSD(T) Be-Be distances for Be<sub>2</sub>, 2.528 Å, and Be<sub>2</sub><sup>-</sup>, 2.434 Å, except for the CCSDT column, where CCSDT Be-Be distances for Be<sub>2</sub>, 2.511 Å, and Be<sub>2</sub><sup>-</sup>, 2.433 Å, are used.

<sup>b</sup>CCSD(T) Be-Be distances for Be<sub>3</sub>, 2.221 Å, and Be<sub>3</sub><sup>-</sup>, 2.113 Å.

level of presented results corresponds to the CCSD(T) approach.<sup>45</sup> As follows from the data, there is a gradual increase of the negative ground state energy,  $E_0$ , with an increasing account of electron correlation in employed methods for both neutral and anionic clusters. The gradual increase of  $E_0$  takes place up to CCSD(T) and CCSDT levels of theory, while the difference between the CCSD(T) values and the more precise CCSDT values for Be<sub>2</sub> is rather small. These results manifest a good convergence and stability of employed calculation methods for neutral and anionic beryllium clusters.

The obtained values of EAs are quite large at all levels of theory. The VEDE for Be<sub>2</sub> at the most precise CCSDT level is 0.341 eV with the 6-311+*G*(3*d2f*) basis set; for Be<sub>3</sub> (D<sub>3h</sub>) it is 1.488 eV at the CCSD(T) level for the same basis set. The CCSDT value for the VEDE of Be<sub>3</sub> (D<sub>3h</sub>) obtained with the 6-311+*G*(3*d2f*) basis set at the CCSD(T) geometry is 1.47 eV. The close agreement between these two last results provides additional confirmation of the stability and convergence of the employed methodology. Bauschlicher and Partridge,<sup>30</sup> using the CASSCF CI approach, have obtained VEA=0.44 eV for Be<sub>2</sub><sup>-</sup> in the <sup>2</sup>Σ<sub>g</sub><sup>+</sup> state. This value coincides with our MP2 value. As follows from Table II, a more complete treatment of electron correlation diminishes the magnitude of EAs for Be<sub>2</sub>. In the Be<sub>3</sub> case, the dependence of the EA upon the electron correlation account is more complex.

The anions of Be<sub>*n*</sub> were observed experimentally by Middleton and Klein.<sup>56</sup> They measured relative intensities of the negative ions of beryllium clusters and came to conclusion that Be<sub>2</sub><sup>-</sup> is definitely metastable with a lifetime >180 μs, while Be<sub>3</sub><sup>-</sup> is either stable or has a lifetime of >500 μs. Our calculations indicate both negative ions Be<sub>2</sub><sup>-</sup> and Be<sub>3</sub><sup>-</sup>, observed in Ref. 56, are stable.

To study the nature of electron attachment to Be<sub>*n*</sub> clusters, we decomposed the electron binding energy into three components, according to Eq. (2). The physical sense of each contribution is described in Sec. II. In Table III, we present the decomposition of the VEA in the ground state of beryllium dimer and two trimer isomers calculated at the CCSD(T) level. For comparison, the same decomposition is

presented for some dipole-bound anions studied in Refs. 16 and 18.

As follows from Table III, the relative magnitude of decomposition components is qualitatively different for each of the studied beryllium clusters. In Be<sub>2</sub><sup>-</sup>, the electrostatic and exchange interactions, described by the Koopmans  $\Delta E_e^{\text{KT}}$  energy, play a destabilizing role. The correlation effects also destabilize the electron binding in the anion. The only factor of stabilization of the excess electron in the Be<sub>2</sub> anion is the relaxation energy, which includes induction and exchange energies at the SCF level. One of possible reasons can be a specific nature of the beryllium dimer bonding: Be<sub>2</sub> is a van der Waals molecule stabilized by the electron correlation energy.<sup>35,23</sup>

Exchange interactions between closed-subshell atoms are always repulsive. Electron correlation effects are necessary to stabilize Be<sub>2</sub>. At large distances, the two-body correlation energy coincides with the dispersion energy.<sup>23</sup> This is why Be<sub>2</sub> can be considered to be a van der Waals dimer. In principle, one can consider bonding with promotion of one 2*s* electron in Be to the vacant 2*p* orbital. Among the lower states that can be formed by two Be atoms in the 2*s*2*p* configuration are singlet <sup>1</sup>Σ<sub>g</sub><sup>+</sup>, and triplet <sup>3</sup>Σ<sub>u</sub><sup>+</sup> and <sup>3</sup>Σ<sub>g</sub><sup>-</sup> states. These states have energies much higher than the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> Be<sub>2</sub> ground state energy. According to our calculations on the lowest triplet state <sup>3</sup>Σ<sub>u</sub><sup>+</sup>, the difference is 0.928 eV. The experimental binding energy of Be<sub>2</sub> is 0.098 eV.<sup>57</sup> Thus, the

TABLE III. Decomposition of the VEA in the ground state of Be<sub>2</sub> and Be<sub>3</sub> calculated at the CCSD(T) level. For comparison, the same decomposition is presented for some dipole-bound anions calculated in Refs. 16 and 18. All energies are in electron volts.

	μ <sup>MP2</sup> , D	ΔE <sub>e</sub> <sup>KT</sup>	ΔE <sub>relax</sub> <sup>SCF</sup>	ΔE <sub>e</sub> <sup>corr</sup>	VEA
Be <sub>2</sub> <sup>-</sup>	0	-0.249	0.606	-0.041	0.316
Be <sub>3</sub> <sup>-</sup> D <sub>3h</sub>	0	0.132	0.552	0.693	1.377
Be <sub>3</sub> <sup>-</sup> D <sub>∞h</sub>	0	0.588	0.955	-1.064	0.480
HCN <sup>16</sup>	3.03	0.0017	0.000 074	-0.000 64	0.0011
C <sub>3</sub> H <sub>2</sub> <sup>-16</sup>	4.48	0.0068	0.000 87	0.0136	0.0214
(HCN) <sub>2</sub> <sup>-18</sup>	6.88	0.058	0.0058	-0.000 37	0.0633

unpairing of the  $2s$  subshell in Be is energetically very unfavorable.

The bonding picture in the beryllium trimers is much more complicated. In Refs. 35, 23, and 24 it was analyzed for the planar  $D_{3h}$   $\text{Be}_3$ . It was shown that so-called three-body forces, representing three-center interactions, play the crucial role in  $\text{Be}_3$  stability. The binding in planar  $\text{Be}_3$  cannot be reduced to a simple sum of three Be–Be bonds and has a large three-body contribution. In contrast to the two-body exchange repulsion, the three-body exchange interaction is attractive. At the SCF level, the three-body exchange attraction is less than the two-body exchange repulsion and  $\text{Be}_3$  is unstable. A sufficiently large  $p$  population revealed in  $\text{Be}_3$  at the SCF level<sup>23</sup> does not provide binding. The latter appears with electron correlation. The two-body correlation attraction completely compensates the two-body exchange repulsion and one can say that three-body delocalized exchange forces are responsible for stabilizing  $\text{Be}_3$ . These forces, as follows from the density difference maps,<sup>24</sup> provide valence-type bonding with  $\pi$ -in-plane character.

As we discussed earlier, both the two-center and three-center interactions are important for  $D_{3h}$   $\text{Be}_3$  stability. This is the reason that in the planar  $D_{3h}$   $\text{Be}_3^-$  anion, all three components of decomposition (2) contribute to the electron binding energy. The dominant contributions to the VEA come from the correlation and relaxation effects. The  $\Delta E_e^{\text{KT}}$  contributes only 10% of the electron binding energy. Thus, it is mainly the dispersion and induction interactions that stabilize the attached electron in the  $\text{Be}_3^-$  ( $D_{3h}$ ) isomer.

The picture is changed in the linear  $D_{\infty h}$   $\text{Be}_3^-$ . Positive contributions to the VEA originate only from relaxation effects and the Koopmans  $\Delta E_e^{\text{KT}}$ . Due to the large negative value of the correlation contribution, the magnitude of the VEA is almost three times smaller than that in the planar  $D_{3h}$  conformation. As we see, in linear  $\text{Be}_3^-$ , as is in  $\text{Be}_2^-$ , the correlation contribution is negative and diminishes the EA. The same situation takes place in the linear dipole-bound anions; see Table III and Ref. 18.

Thus, the correlation contribution diminishes the magnitude of the electron binding energy in linear molecules, destabilizing the anion formation. On the other hand, the electron correlation stabilizes molecular systems, and this effect takes place for both neutral and charged systems. To solve this apparent paradox, we have to recall that the electron binding energy,  $\Delta E_e$ , is defined as a differential characteristic and the same is true for  $\Delta E_e^{\text{corr}}$  [see Eq. (8)]. Both terms in Eq. (8) are negative. The negative value of  $\Delta E_e^{\text{corr}}$  means that the electron correlation contribution to a neutral molecule,  $\Delta E_{\text{corr}}(N)$ , is larger than the same contribution,  $\Delta E_{\text{corr}}(N+1)$ , to its anion. In other words, the correlation effects in neutral linear molecules are more important than in their linear anions. This is conformed by the calculated electron correlation energies of beryllium clusters and their anions presented in Table IV. Only in the planar  $D_{3h}$   $\text{Be}_3$ , the electron correlation contribution to the ground state energy is larger in an anion than in a neutral cluster. As a result, the correlation contribution to the AEA of  $\text{Be}_3$  ( $D_{3h}$ ) is about 50% of its total value.

Although all studied beryllium clusters possess a quad-

TABLE IV. Correlation contributions to the CCSD(T) ground state energies ( $\Delta E_{\text{corr}}$ ) and adiabatic electron affinities ( $\Delta E_e^{\text{corr}}$ ), in electron volts.

	$\Delta E_{\text{corr}}$	$\Delta E_e^{\text{corr}}$
$\text{Be}_2$	-2.811	
$\text{Be}_2^-$	-2.788	-0.023
$\text{Be}_3$ $D_{3h}$	-4.682	
$\text{Be}_3^-$ $D_{3h}$	-5.415	0.733
$\text{Be}_3$ $D_{\infty h}$	-5.102	
$\text{Be}_3^-$ $D_{\infty h}$	-4.038	-1.064

<sup>a</sup>At the neutral  $\text{Be}_3$   $D_{\infty h}$  geometry.

rupole moment, the small value of  $\Delta E_e^{\text{KT}}$  in  $\text{Be}_3^-$  ( $D_{3h}$ ) and even a negative one in  $\text{Be}_2^-$  indicate that these anions are not quadrupole bound. The quadrupole moment can be partly involved in the binding in  $\text{Be}_3^-$  ( $D_{\infty h}$ ), although the relaxation energy is more important for the electron stabilization in this anion and it is the single stabilization factor in  $\text{Be}_2^-$ . The largest electron binding energy is revealed in the planar  $D_{3h}$  beryllium trimer and is provided by the correlation and relaxation contributions.

As follows from Table III, the values of VEAs obtained in  $\text{Be}_2$  and  $\text{Be}_3$  clusters are between 10 and  $10^3$  times larger than the VEAs in the dipole-bound anions. This strongly suggests that in beryllium anions an excess electron occupies a valence vacant orbital and beryllium anions may be considered as valence-bound, as in some metastable anions of uracil<sup>58</sup> and cytosine.<sup>59</sup> Plots of the highest occupied orbitals of the anions, shown in Figs. 1 and 2, disclose the dominant valence character of the change in electronic structure between molecules and corresponding anions. The lowest, virtual, canonical HF orbitals of the neutrals consist chiefly of valence  $s$  and  $p$  basis functions. Singly occupied spin orbitals that occur only in UHF calculations on anions are composed of the same atomic functions. Both types of these one-electron functions may be considered approximations to the Dyson orbitals<sup>60</sup> corresponding to the electron affinities of the Be clusters. In the first case, neglect of relaxation and correlation effects is likely to produce an approximate Dyson orbital that is too diffuse, while in the second case, the approximate Dyson orbital is likely to be too contracted. Therefore, relaxation effects, while important in determining electron affinities, do not produce qualitative changes in the Dyson orbital associated with electron attachment to the neutral species.

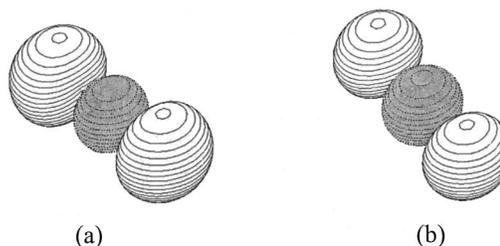


FIG. 1. Molecular orbital diagrams of  $\text{Be}_2$  and  $\text{Be}_2^-$ : (a)  $\text{Be}_2$  LUMO,  $3\sigma_g$  and (b)  $\text{Be}_2^-$  SOMO,  $3\sigma_g$ .

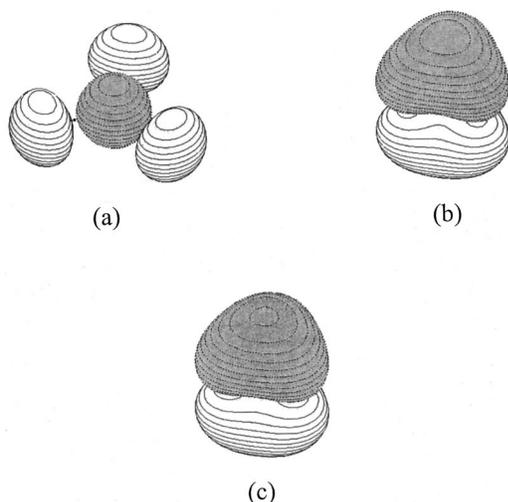


FIG. 2. Molecular orbital diagrams of  ${}^1A'_1$   $\text{Be}_3$  and  ${}^2A''_2$   $\text{Be}_3^-$ : (a)  $\text{Be}_3$  LUMO,  $3a'_1$ ; (b)  $\text{Be}_3$  LUMO+1,  $1a''_2$ ; and (c)  $\text{Be}_3^-$  SOMO,  $1a''_2$ .

#### IV. CONCLUSIONS

As follows from molecular orbital diagrams and high values of EAs, all studied beryllium anions are valence bound. The decomposition of the electron binding energy indicates a different nature of binding in  $\text{Be}_2^-$  and the two  $\text{Be}_3^-$  isomers. In  $\text{Be}_2^-$ , the only factor of stabilization of the excess electron is the relaxation energy. In the linear  $\text{Be}_3^-$ , the electrostatic quadrupole interactions contribute to the binding, although the relaxation energy is still more important for its stabilization. In the most stable  $\text{Be}_3^-$  ( $D_{3h}$ ) anion, the dominant contributions to the electron attachment energy are provided by the correlation and relaxation energies. At large distances, these energies reduce to the dispersion and induction energies between the excess electron and the neutral beryllium trimer, but in anions they cannot be separated from exchange and overlap effects.

As was revealed in our study, in the linear molecules considered, the correlation contribution to the electron binding energy is negative, i.e., it diminishes the EA. It can be explained, if we consider the representation of  $\Delta E_e^{\text{corr}}$  as a difference of two electron correlation energies, Eq. (8). Although the electron correlation effects stabilize both neutral and negatively charged molecules, the electron correlation contribution in neutral linear molecules is larger than in their linear anions (see Table IV).

The obtained values of EAs are quite large at all levels of theory. The VEDE in  $\text{Be}_2^-$  is 0.341 eV and is more than four times larger in  $\text{Be}_3^-$  ( $D_{3h}$ ): 1.488 eV at the CCSD(T) level and 1.470 eV at the CCSDT level (with a little smaller basis set). This is a clear indication of the stability of these anions. To the best of our knowledge, there are no published experimental data of electron affinities of beryllium clusters. It is important to obtain an experimental verification of our theoretical predictions.

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- <sup>1</sup>F. Fermi and E. Teller, Phys. Rev. **72**, 399 (1947).
- <sup>2</sup>O. H. Crawford, Proc. R. Soc. London **91**, 279 (1967).
- <sup>3</sup>W. B. Brown and R. E. Roberts, J. Chem. Phys. **46**, 2006 (1967).
- <sup>4</sup>J. Simons, Annu. Rev. Phys. Chem. **28**, 15 (1977).
- <sup>5</sup>W. R. Garrett, J. Chem. Phys. **73**, 5721 (1980); **77**, 3666 (1982).
- <sup>6</sup>J. Simons and K. D. Jordan, Chem. Rev. **87**, 535 (1987).
- <sup>7</sup>L. Adamowicz and R. J. Bartlett, J. Chem. Phys. **88**, 313 (1988).
- <sup>8</sup>D. R. Bates, Adv. At., Mol., Opt. Phys. **27**, 1 (1991).
- <sup>9</sup>J. Kalcher and A. F. Sax, Chem. Rev. **94**, 2219 (1994).
- <sup>10</sup>C. Desfrancois, H. Abdoul-Carime, N. Khelifa and J. P. Shermann, Phys. Rev. Lett. **73**, 2436 (1994).
- <sup>11</sup>G. L. Gutsev and L. Adamowicz, J. Phys. Chem. **102**, 9309 (1995).
- <sup>12</sup>G. L. Gutsev and R. J. Bartlett, J. Chem. Phys. **105**, 8785 (1996).
- <sup>13</sup>M. Gutowski, P. Skurski, A. I. Boldyrev, J. Simons, and K. D. Jordan, Phys. Rev. A **54**, 1906 (1996).
- <sup>14</sup>M. Gutowski and P. Skurski, J. Phys. Chem. B **101**, 9143 (1997).
- <sup>15</sup>M. Gutowski, P. Skurski, K. D. Jordan, and J. Simons, Int. J. Quantum Chem. **64**, 183 (1997).
- <sup>16</sup>M. Gutowski, K. D. Jordan, and P. Skurski, J. Phys. Chem. A **102**, 2624 (1998).
- <sup>17</sup>H. Abdoul-Carime and C. Desfrancois, Eur. Phys. J. D **2**, 149 (1998).
- <sup>18</sup>M. Gutowski and P. Skurski, Chem. Phys. Lett. **300**, 331 (1999).
- <sup>19</sup>F. Wang and K. D. Jordan, J. Chem. Phys. **114**, 10717 (2001).
- <sup>20</sup>J. Simons and P. Skurski, Recent Res. Devel. Phys. Chemistry, Research Signpost, Trivandrum, 2001.
- <sup>21</sup>T. Koopmans, Physica E (Amsterdam) **1**, 104 (1934).
- <sup>22</sup>I. G. Kaplan, *Theory of Molecular Interactions* (Elsevier, Amsterdam, 1986).
- <sup>23</sup>I. G. Kaplan, S. Roszak, and J. Leszczynski, J. Chem. Phys. **113**, 6245 (2000).
- <sup>24</sup>I. G. Kaplan, S. Roszak, and J. Leszczynski, Adv. Quantum Chem. **40**, 257 (2001).
- <sup>25</sup>P. Kristensen, V. V. Petrunin, H. H. Andersen, and T. Andersen, Phys. Rev. A **52**, R2508 (1995).
- <sup>26</sup>J.-J. Hsu and K. T. Chung, Phys. Rev. A **52**, R898 (1995).
- <sup>27</sup>K. D. Jordan and J. Simons, J. Chem. Phys. **65**, 1601 (1976).
- <sup>28</sup>K. D. Jordan and J. Simons, J. Chem. Phys. **67**, 4027 (1977).
- <sup>29</sup>K. D. Jordan and J. Simons, J. Chem. Phys. **77**, 5250 (1982).
- <sup>30</sup>C. W. Bauschlicher, Jr. and H. Partridge, J. Chem. Phys. **80**, 334 (1984).
- <sup>31</sup>R. J. Harrison and N. C. Handy, Chem. Phys. Lett. **123**, 321 (1986).
- <sup>32</sup>R. J. Bartlett, J. P. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).
- <sup>33</sup>J. D. Watts, I. Cernusak, I. Noga, R. J. Bartlett, C. W. Bauschlicher, Jr., T. J. Lee, A. P. Rendell, and P. Taylor, J. Chem. Phys. **93**, 8875 (1990).
- <sup>34</sup>W. A. Shirley and G. A. Peterson, Chem. Phys. Lett. **181**, 588 (1991).
- <sup>35</sup>I. G. Kaplan, J. Hernández-Cobos, I. Ortega-Blake, and O. Novaro, Phys. Rev. A **53**, 2493 (1996).
- <sup>36</sup>I. Røeggen and J. Almlöf, Int. J. Quantum Chem. **60**, 453 (1996).
- <sup>37</sup>J. Stárck and W. Meyer, Chem. Phys. Lett. **258**, 421 (1996).
- <sup>38</sup>J. M. L. Martin, Chem. Phys. Lett. **303**, 399 (1999).
- <sup>39</sup>R. J. Gdanitz, Chem. Phys. Lett. **312**, 578 (1999).
- <sup>40</sup>P. O. Löwdin, Adv. Chem. Phys. **2**, 207 (1959).
- <sup>41</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 99, Development version (Revision B.06+) Gaussian, Inc., Pittsburgh, PA, 1998.
- <sup>42</sup>J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, Int. J. Quantum Chem., Symp. **26**, 879 (1992).
- <sup>43</sup>ACES II, program product of the Quantum Theory Project, University of Florida, J. F. Stanton, J. Gauss, J. D. Watts *et al.*, Integral packages included are VMOL (J. Almlöf and P. R. Taylor); VPROPS (P. R. Taylor); and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor).

- <sup>44</sup>G. Schaftenaar, MOLDEN, version 3.4 (CAOS/CAMM Center, the Netherlands, 1998).
- <sup>45</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
- <sup>46</sup>R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
- <sup>47</sup>T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. von R. Schleyer, J. Comput. Chem. **4**, 294 (1983).
- <sup>48</sup>M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).
- <sup>49</sup>J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).
- <sup>50</sup>G. E. Scuseria and H. F. Schaefer III, Chem. Phys. Lett. **152**, 382 (1988).
- <sup>51</sup>J. D. Watts and R. J. Bartlett, J. Chem. Phys. **93**, 6104 (1990).
- <sup>52</sup>H. B. Schlegel, J. Chem. Phys. **84**, 4530 (1986).
- <sup>53</sup>R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
- <sup>54</sup>D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **100**, 2975 (1994).
- <sup>55</sup>cc-pVQZ exponents and coefficients for Be were taken from the MOLPRO website, [www.tc.bham.ac.uk/molpro](http://www.tc.bham.ac.uk/molpro)
- <sup>56</sup>R. Middleton and J. Klein, Phys. Rev. A **60**, 3786 (1999).
- <sup>57</sup>V. E. Bondybey, Chem. Phys. Lett. **109**, 436 (1984).
- <sup>58</sup>O. Dolgounitcheva, V. G. Zakrzewski, and J. V. Ortiz, Chem. Phys. Lett. **307**, 220 (1999).
- <sup>59</sup>O. Dolgounitcheva, V. G. Zakrzewski, and J. V. Ortiz, J. Phys. Chem. A **105**, 8782 (2001).
- <sup>60</sup>J. V. Ortiz, Adv. Quantum Chem. **35**, 33 (1999).