Non-additivity of intermolecular forces in helium and beryllium clusters

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Abstract: New results on nonadditive effects on small beryllium clusters are presented using the LCAO-MO-SCF method including variational and perturbational (MP-4) configuration effects. Three- and four-body contributions to the interaction energy of these clusters are dominant, and are used to explain the very different behaviour of bulk beryllium as compared to liquid helium. This is relevant because the atomic ground states of Be and He are strikingly similar (1s²2s¹, 1s¹2s¹, and 1s³) and also He₂ and Be₂ share the honour of being the two hardest-to-detect dimers in the whole periodic system. The similarity is lost for larger Heₙ and Beₙ systems because the former, as was shown by R.F.W. Bader 25 years ago, have very small three-body energies (≤1%). Beₙ clusters will be shown here to have three-body energies that actually outweigh the pairwise additive ones. The consequences of this are discussed.

Key words: intermolecular forces, non-additivity, He and Be clusters.

Introduction

Certainly the hardest-to-detect elementary dimers are He₂ and Be₂. As recently as 1984 Bondybey (1) could correctly state bound state, in fact) is even more recent (2, 3). This makes the more so than any other noble gas dimer. In fact, a recent study hand, the bulk properties of beryllium, a semi-metal, are completely different from those of the noble gases, with the case of three-body effects of the ~e(2s') to the following question: why do the similarities found in large aggregates of these elements? The answer lies in the three-body effects of the Be₃ versus the He₃, Ne₃, etc. trimers, as we shall try to show here.

The first fully ab-initio study of three-body nonadditive effects was carried out by R.F.W. Bader et al. (6) (the definition of nonadditive contributions to the energy will be discussed in the following section). They reached the following conclusion: nonadditive contributions to the energy of He₃ calculated at the LCAO-MO-SCF level of approximation, were 10 times larger than estimated before by perturbation treatments (7). Still, their relative role in He₃ binding was at most a few percent of the pairwise additive contributions (6). KoCós and LeC (8) confirmed these results to be valid at the Hartree–Fock limit. The convergence of the many-body expansion for Heₙ clusters was first tested by Novaro and Beltrán-López (9) at this same level of accuracy. Much more recently, high level ab-initio calculations (910) have again confirmed that many-body nonadditive interactions are a few percent of the pairwise additive contributions for small Heₙ clusters.

As concerns Be₃ and Be₄, they were studied by Novaro and KoCós (11), also at the LCAO-MO-SCF level, who found that nonadditive effects were quite large, large enough in fact to make the convergence of the many-body expansion (see following section) doubtful at best. We here present recent results (12) at the CI level for Beₙ clusters that confirm that the main difference between bulk He and Be is based on their non-additive energies.

Method

In the quantum mechanical study of the total energy of an n-
particle system, the interaction energy is computed as the total
energy of the system minus the energy of its constituents:

\[ E_{\text{int}}(n) = E(n) - \sum_{i=1}^{n} E_i \]

where \( E_i \) is the calculated energy (at the same level of preci-
sion as the calculation of \( E(n) \)) for the \( i \)th particle of the system.
The interaction energy \( E_{\text{int}}(n) \) in turn can be divided in terms of
different order interactions within the system. One can define
the interactions between pairs, triplets, etc. up to interactions
involving \( n \) particles simultaneously. By defining the sum of
the calculated energies of the \( n \) individual particles as the one-
body energy:

\[ E_1(n) = \sum_{i=1}^{n} E_i \]

we can go on to define the two-body energy of the system as:

\[ E_2(n) = \sum_{i<j}^{[n]} E_{ij} \]

the three-body energy as:

\[ E_3(n) = \sum_{i<j<k}^{[n]} E_{ijk} \]

the four-body energy as:

\[ E_4(n) = \sum_{i<j<k<l}^{[n]} E_{ijkl} \]

To obtain \( E_3(n) \) we sum up the interaction energy of all pairs
from which the individual particle energies are subtracted. To
obtain \( E_2(n) \) we similarly add the interactions of all triplets
from which the component pair and individual particle ener-
gies are subtracted, and so on. Through these definitions the
interaction energy of an \( n \)-particle system can be expressed as
a finite sum

\[ E_{\text{int}}(n) = E_2(n) + E_3(n) + E_4(n) + \ldots + E_n(n) \]

This is the many-body expansion of the interaction energy and
it will be considered to be convergent if the higher order terms
are systematically smaller than the lower order terms. In fact,
in many applications to study large aggregates, the hypothesis
that \( E_3(n) \) and higher terms are negligible with respect to \( E_2(n) \)
is postulated uncritically.

We here, on the contrary, want to calculate \( E_3(n) \), etc. with
the highest possible precision. We must stress that eq. [6] pro-
vides an exact representation of the interaction energy of an \( n \)-
particle system. Only the level of approximation with which
the different terms are calculated limits the precision within
\( E_{\text{int}}(n) \) is given.

For the case of small Be and Li clusters, previous calcula-
tions at the SCF level already exist for the multibody expan-
sion. To go beyond the SCF level we here use the Möller-
Plesset perturbation theory approximation to the correlation
energy corrections. We do these calculations utilizing the
Gaussian-92 program (13) on UNAM's Cray-YMP4/468
computer. The basis set used is the Gaussian-92 internal 6-311+G(3df)
having one diffuse p-function, three 5d-functions,
and one 7f-function. The frozen-core approximation of the
correlation energy is obtained at the fourth-order Möller-
Plesset approximation.

In reality the computational cost added to the calculation of
the total energy of an \( n \)-particle system by calculating its dif-
fferent \( m \)-body contributions given in eq. [6] is not high
because \( m \leq n \) and \( E_m(n) \) implies much less computer memory
than \( E(n) \) itself. On the other hand, the individual \( m \)-body
terms contained in the sum:

\[ E_m(n) = \sum_{i<j<k< \ldots <l}^{[n]} E_{ij \ldots l} \]

all have different geometries so several configurations for the
triplets, quartets, etc. have to be calculated.

Results

Using the method described in the preceding section, we cal-
culated the interaction energies of the Be\(_2\), Be\(_3\), Be\(_4\), and Li\(_2\),
Li\(_3\), Li\(_4\) systems as well as their pairwise additive and many-
body nonadditive contributions. These energies are given in
Table 1. The first thing we notice is that the Be dimer is very
slightly bound, especially compared to the Li dimer. This is
also evident in Fig. 1, which shows for Li\(_2\) a deep potential
energy well with steep walls towards both the united-atom and
the separated-atom limits. For Be\(_2\), in contrast, a very shallow
well, as well as a very flat potential energy curve, is evident. In
fact, the Be\(_2\) curve resembles noble gas dimer curves, very dif-
f erent from that of Li\(_2\).

But as we look at the other numbers in
Table 1, the differences between beryllium and lithium seem-
ingly diminish. As concerns the interaction energy, for Be\(_3\) it
already is quite similar to that for Li\(_3\), and for Be\(_4\), in fact, it is
even more attractive than for Li\(_4\).

Also notable is the very poor convergence of the many-
body expansion for both lithium and beryllium. In Li\(_3\) three-
body repulsions already cancel over 50% of the pair attrac-
tions. Li\(_4\) is even more extreme as \( E_3(n) \) is larger in magnitude

Fig. 1. Potential energy curves for the beryllium and lithium dimers.
becomes evident that for larger clusters higher order terms in the many-body expansion will always dominate. For Be$_3$, almost all of the interaction energy $E(n)$ comes from the three-body term. As would be expected from the noble-gas-like potential energy curve for Be$_3$, pairwise attractions are always very small; it is only the comparatively large three-body attractions that make Be$_3$ stable, with some 20 times larger binding energy than Be$_2$. In the case of Be$_4$ this is even more evident as all of the stabilization is due to three-body attractions. The pairwise term in fact is repulsive. This means simply that the equilibrium positions of the four beryllium nuclei are determined by the strong three-body attractions, making the inscribed dimers somewhat short, so short that each Be–Be distance falls on the repulsive part of the curve in Fig. 1. But even these pair repulsions are smaller than the repulsive four-body term. The main result, however, is that for Be$_4$ clusters the stabilization comes entirely from three-body interactions. We can safely generalize: Be$_n$ clusters are primarily determined by nonadditive effects. This is in absolute contrast with He$_n$ clusters for which nonadditive effects are very small. We shall see the consequences of this in the following section.

### Discussion

We have seen that nonadditive contributions to the binding energy of the smallest Be$_n$ clusters ($n \geq 3$) are decisive. For medium-size clusters ($n \geq 5$) one can observe the fact that three-body contributions to the total binding energy are larger than pairwise (two-body) contributions has become a rule, rather than an exception. Let us pause for a moment to consider the consequences of this fact. Two-body energies are directly associated with the chemical bond between two individual partners in a given cluster. Three-body energies are not localized on a particular bond. They really correspond to the change in the distance and the energy of any bond between two partners introduced by a third one. They are by their very definition delocalized. The fact that three-body terms are so large in beryllium has great consequences.

For helium, we have known since the work of Bader et al. (6) that three-body effects, while non-negligible, are a small correction to the total energy. Thus we may conclude that the “weakest and weakest molecular bond (4): He$_n$” may only lead to the very weakly bound bulk behaviour of liquid helium even at temperatures near 0 K.

The second weakest elementary chemical bond, Be$_2$, does not prepare us for the bulk beryllium metal properties at room temperature. This is because Be$_2$ does not contain the main cause of the metal stability: the quite large three-body energy appears only for beryllium trimers and beyond. Dominant in size, delocalized in nature, it is in essence the image of a metallic bond-in-the-making even for the small Be$_3$, Be$_4$ molecules.

Although the language of nonadditivity is not too familiar, what we have concluded above is of course not a new concept. We have seen in the previous section, for instance, that the nonadditivity for Li$_n$ clusters is also quite large. We could make a parallel discussion about H and Li, with apparently quite indistinguishable and $(1s^1$, and $1s^22s^1:2p_{2s1}^2$) ground states. Yet H$_2$ is tightly bound while H$_3$ is very unstable. In contrast, the change from Li$_2$ to Li$_3$ and beyond is only a straightforward tendency to the classical metal bond in lithium. The argument of the presence of the empty $2p^0$ subshell in Li in regard to this tendency is too well known to merit any further comment here. Naturally, for Be the $2p^0$ subshell should play a quite similar role.

In short, the answer to our original question: since He$_2$ and Be$_2$ have similar bonding properties, why are bulk beryllium and helium so utterly different? has an obvious answer. The many body effects are very different in both cases. By the expression “many-body effects” we are not speaking of $10^{24}$ particles interacting. We in fact are referring to much smaller system. Many-body effects are already dominant for the small “metallic” Be$_3$ and Li$_3$ clusters.

### Acknowledgements

A quarter of a century has elapsed since I met Richard Bader during his first trip to Mexico, invited by our mutual friend Virgilio Beltrán. For a person with a fresh Ph.D. and new research responsibilities and projects, it was an invaluable and invigorating experience to collaborate with Richard, a brilliant and enthusiastic scientist with whom we established the first ab-initio study of three-body nonadditive effects. His impressive energy (even though he was particularly sensitive to the high altitude of Mexico City) and the pleasure of sharing quality moments with our families linger on in my memory. Even though I have since pursued other fields of research, my
curiosity about nonadditive effects has not waned and in fact it has given me the chance of collaborating with several friends in different countries, like John Murrell, Włodek KoČos, Ludwig Bruch, Feng Wen-Lin, Enrico Clementi, Ilya Kaplan, and others. Curiously, with Richard Bader our opportunities for scientific and even personal contacts have been scarce. My loss. I always, however, have followed his many successes in research and his growing scientific stature and my admiration for him is ever increasing. I sincerely congratulate the authors of this initiative to honour Richard Bader and hope that this very modest contribution on my part to this special volume of the Canadian Journal of Chemistry serves to add my sincere homage to this exceptional scientist and friend.

I would also like to thank Ilya Kaplan and Jorge Hernández for the use of the beryllium results that will appear in more extended form in a joint paper. To Ilya I am further indebted for his reading of and comments on this manuscript and, in general, for his unselfish help. I also acknowledge financial support from Conacyt and DGAPA to this line of research.

References