

Ab initio model potentials for the alkaline-earth trimers Be₃, Mg₃, and Ca₃

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Many-body model potentials for Be₃, Mg₃, and Ca₃ clusters have been constructed with parameters fitted to the corresponding *ab initio* many-body energy surfaces calculated at the MP4 (SDTQ) level. These *ab initio* model potentials are accurate over a wide range of atom–atom distances, and are suitable for molecular dynamics simulation, collision dynamics, and other physical applications.

1. Introduction

In recent years, atomic and molecular clusters have become one of the most active fields of experimental and theoretical research [1–4]. Clusters can be considered as a bridge between molecules and condensed matter, and the study of so-called dimensional effects [5, 6] may allow us to understand how the microscopic properties evolve towards macroscopic ones. Clusters also attract special attention because of their technological importance in such fields as materials science and heterogeneous catalysis.

The study of binding in alkaline-earth clusters has special interest. These atoms have a closed outer subshell ns^2 , so they have no valence electrons in their ground state, but in contrast to the noble gas atoms that form very weak bonded clusters, and even in the bulk have such small cohesive energy that they are able to form solids only at low temperatures, the alkaline-earth atoms form stable clusters with binding energy rapidly increasing with the number of atoms in the cluster [7, 8]. The cohesive energy in alkaline-earth solids is two to three times larger than that in solids of the one ns -valence alkaline elements (see Kittel [9]).

As was shown by Kolos *et al.* [10] and established by precise calculations at the electron correlation level

[7, 8, 11], the three-body forces play a crucial role in alkaline-earth cluster stability. More detailed studies, based on the decomposition of the many-body interaction energies into physical components [8, 12], revealed that primarily the alkaline-earth trimers are stabilized by the 2-body dispersion forces and 3-body exchange forces.

The analysis of these physical contributions to the interaction energy allows one to choose suitable analytical forms for a model potential, and the parameters of each part can be fitted separately to the corresponding parts of the interaction energy. Such model potentials have been called *ab initio* model potentials [13] (in contrast to semi-empirical model potentials). The procedure for constructing such potentials for metal clusters has been elaborated in [13–16].

With the assumption that many-body contributions to the potential become unimportant beyond 3-body terms, then such analytical potentials, which are accurate over the physically realistic configuration space, can be used for Monte Carlo or molecular dynamics simulations of clusters and condensed matter, in collision dynamics, and in spectroscopic studies. For example, in [13, 16], an *ab initio* model potential was utilized in the molecular dynamics simulation studies of the thermal stability of silver clusters.

In the present paper, we construct *ab initio* model potentials for Be, Mg, and Ca trimers with parameters

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fitted to the ground state potential surfaces calculated at the MP4(SDTQ) level [8]. The fitting procedure used in the study is a little different from that used in [15], where an *ab initio* model potential for the beryllium trimer was obtained. In the current work, the parameters in the dispersion and exchange parts of the 2-body potential function have been fitted separately, and the 3-body dispersion parameter C_9 has been taken from the best independent calculation [17]. For the 2-body exchange potential function, we have used a more accurate five-parameter function instead of the two-parameter exponential expression used in [15].

The *ab initio* data which we use provide a wide coverage of the potential energy surfaces, and in these calculations an attempt was made to obtain comparable levels of accuracy for the triatomic molecules and their diatomic dissociation products.

2. Theory and discussion

All the *ab initio* data used [8] were obtained from the Gaussian98 code [18] with Møller–Plesset perturbation theory up to fourth order, MP4 (SDTQ), in the frozen core approximation. A standard 6-311 + G(3df) basis set [19] was used. This is a triple-split valence basis set, having one diffuse p function, three 5d functions and one 7f function.

In variational methods, the interaction energy is not calculated directly. The same situation takes place in the frame of Møller–Plesset perturbation theory. We calculated the interaction energy at all calculation levels as a difference

$$E_{\text{int}}(N) = E(N) - NE_a \quad (1)$$

where $E(N)$ is the total energy of cluster A_N and E_a is the atomic energy calculated at the same level of accuracy as $E(N)$. Taking into account the basis set superposition error, the atomic energy in equation (1) was calculated using the dimer basis set for $N = 2$ and the trimer basis set for $N = 3$.

According to its definition, the electron correlation energy at the MP4 level is

$$\Delta E_{\text{int}}^{\text{corr}} = E_{\text{int}}^{\text{MP4}} - E_{\text{int}}^{\text{SCF}} = \sum_{n=2}^4 \varepsilon_{\text{MP}}^{(n)}. \quad (2)$$

To check the convergence of the MP perturbation series it is convenient to express the MP series by ratios to the second-order contribution

$$\Delta E_{\text{int}}^{\text{corr}} = \varepsilon_{\text{MP}}^{(2)} \left(1 + \frac{\varepsilon_{\text{MP}}^{(3)}}{\varepsilon_{\text{MP}}^{(2)}} + \frac{\varepsilon_{\text{MP}}^{(4)}}{\varepsilon_{\text{MP}}^{(2)}} \right). \quad (3)$$

At the equilibrium distance, the MP series (equation (3)) have the following forms [8]:

$$\begin{aligned} \text{Be}_2: & \varepsilon_{\text{MP}}^{(2)}(1 + 0.12 + 0.06), \\ \text{Mg}_2: & \varepsilon_{\text{MP}}^{(2)}(1 + 0.14 + 0.03), \\ \text{Ca}_2: & \varepsilon_{\text{MP}}^{(2)}(1 + 0.18 + 0.07). \end{aligned} \quad (4)$$

Thus, limiting the calculations at the MP4 level looks quite justified; we checked that the convergence is satisfactory for all the calculated distances we used.

The many-body decomposition of the interaction energy at different approximations was performed according to the general definition [20]. In the homoeatomic case they are represented by the following formulae:

$$E_2(A_3) = \sum_{a<b} \varepsilon_{ab}, \quad (5)$$

$$\varepsilon_{ab} = E(ab) - 2E_a, \quad (6)$$

where $E(ab)$ is the total energy of two atoms at the same distances they have in the trimer abc . For a general triangle, the sum (5) contains three different 2-body interaction energies. The 3-body energy is defined as a difference

$$E_3(A_3) = E(A_3) - E_2(A_3) - 3E_a, \quad (7)$$

where $E(A_3)$ denotes the total energy of trimer A_3 . Formulae (5)–(7) were used to calculate the 2- and 3-body contributions to the interaction energy at the SCF and MP4 levels, and for the decomposition of the electron correlation energy.

For a three-atom system, the model potential is naturally decomposed into the 2-body and 3-body interaction terms

$$V(\text{ABC}) = V_2 + V_3 = \sum_{a<b} V_{ab} + V_{abc}. \quad (8)$$

Both V_2 and V_3 can be represented as a sum of exchange and dispersion terms. For the 2-body interactions, the Buckingham potential has been widely used for various systems, although it cannot be ground for atoms with open valence shells, forming the covalent bond, because of the attractive nature of exchange interaction in this case. For atoms with closed electron shells or subshells (as in the case of alkaline-earths) the choice of the Buckingham-type potential can be ground. The point is that these atoms have no multipole moments, and their electrostatic and induction interactions have a pure overlap origin, as do the exchange terms. Thus, all these interactions can be represented by a single analytical function with exponential behaviour. At large distances, where overlap between orbitals of the interacting atoms is negligible, only the dispersion forces contribute to the interaction energy.

Thus, the 2-body potential was taken in the Buckingham-type form with dispersion terms up to r^{-10}

Table 1. Comparison of E_2^{disp} (equation (11)), with ΔE^{corr} [8] at equilibrium and for large distances; energies in kcal mol⁻¹.

$r/\text{\AA}$	Be ₂		Mg ₂		Ca ₂	
	E_2^{disp}	ΔE^{corr}	E_2^{disp}	ΔE^{corr}	E_2^{disp}	ΔE^{corr}
2.56	-79.62	-7.94				
3.92			-8.95	-2.27		
4.56					-14.40	-3.19
5.00	-0.35	-0.36	-1.29	-0.87	-6.85	-2.23
6.00	-0.10	-0.11	-0.35	-0.33	-1.68	-0.92
7.00	-0.03	-0.04	-0.11	-0.12	-0.55	-0.39
8.00			-0.04	-0.04	-0.22	-0.17
9.00					-0.10	-0.08
10.00					-0.05	-0.04

and the exchange term multiplied by a polynomial as follows:

$$V_{ab} = (a_0 + a_1 r_{ab} + a_2 r_{ab}^2 + a_3 r_{ab}^3) \exp(-\alpha r_{ab}) - \left(C_6 \frac{D_6(r_{ab})}{r_{ab}^6} + C_8 \frac{D_8(r_{ab})}{r_{ab}^8} + C_{10} \frac{D_{10}(r_{ab})}{r_{ab}^{10}} \right). \quad (9)$$

The damping functions $D_n(r_{ab})$, which improve the behavior of the dispersion energy in the overlap region (see discussion in [15]), were taken in the standard form

$$D_n = \begin{cases} \exp \left[-\beta_n \left(\frac{k_n}{r_{ab}} - 1 \right)^2 \right] & r_{ab} < k_n, \\ 1 & r_{ab} \geq k_n. \end{cases} \quad (10)$$

The same value of k_n was taken for each D_n ; relaxing this condition did not significantly improve the fitting.

The SCF energy contains the electrostatic, exchange, and induction contributions which all were approximated in equation (9) by the exponentially based term; this term was fitted to the SCF energy. The dispersion terms were fitted to the electron correlation energy.

To confirm our calculations for the dispersion energies we examined the long range form

$$E_2^{\text{disp}} = - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right). \quad (11)$$

The dispersion coefficients C_n for the Be, Mg, and Ca atoms have been estimated in [17] by the Padé approximant method. Using the values given there for C_n converted to kcal mol⁻¹ \AA^n units, we found sum (11) at equilibrium and at large distances, and present this in table 1 together with ΔE_{corr} as calculated in [8]. The agreement is seen to be very good for Be₂ for $r \geq 5 \text{\AA}$, for Mg₂ for $r \geq 6 \text{\AA}$, and for Ca₂ for $r \geq 9 \text{\AA}$. This coincidence takes place for quantities calculated by different methods and at different approximations. From this it follows that this is based on physical grounds: the dis-

persion forces (at least in closed shell or subshell atomic systems) have a pure electron correlation origin.

For intermediate distances, where overlap of the atomic valence shells becomes essential, the dispersion forces cannot be defined without allowing for exchange effects, and expression (11) is not valid. The damping functions are introduced to correct for this. Table 1 shows that at equilibrium distances the value of the pure dispersion energy is much larger than ΔE_{corr} (in the case of Be₂ it is 10 times larger).

The 3-body potential also may be expressed by a sum of exchange and dispersion terms:

$$V_{abc} = V_{abc}(\text{exch}) + V_{abc}(\text{disp}). \quad (12)$$

The 3-body exchange terms were based, as in the previous work [15], on the symmetry adapted Q coordinates [21] defined as follows:

$$\begin{aligned} Q_1 &= (r_{ab} + r_{bc} + r_{ca}) / (3)^{1/2}, \\ Q_2 &= (r_{bc} - r_{ca}) / (2)^{1/2} \\ Q_3 &= (2r_{ab} - r_{bc} - r_{ca}) / (6)^{1/2}. \end{aligned} \quad (13)$$

The potentials must be symmetric to exchange of atoms, and this is achieved by using only the totally symmetric combinations

$$Q_1, Q_2^2 + Q_3^2, Q_3^3 - 3Q_3Q_2^2. \quad (14)$$

For C_{2v} geometries ($r_{bc} = r_{ca}$), Q_2 is zero, but because there is only one quadratic and one cubic symmetry combination of Q_2 and Q_3 , fitting points on a Q surface using only C_{2v} geometries will unambiguously determine an expansion in Q_2 and Q_3 up to 5th power; only for higher powers does one need data on C_s geometries. The exchange part of the 3-body term is defined by one exponent and 15 polynomial coefficients as follows

$$\begin{aligned}
V_{abc}(\text{exch}) = & [(b_2 + b_3 Q_1 + b_4 Q_1^2) \\
& + (Q_2^2 + Q_3^2)(b_5 + b_6 Q_1 + b_7 Q_1^2) \\
& + (Q_3^3 - 3Q_3 Q_2^2)(b_8 + b_9 Q_1 + b_{10} Q_1^2) \\
& + (Q_2^2 + Q_3^2)^2(b_{11} + b_{12} Q_1 + b_{13} Q_1^2) \\
& + (Q_2^2 + Q_3^2)(Q_3^3 - 3Q_3 Q_2^2) \\
& \times (b_{14} + b_{15} Q_1 + b_{16} Q_1^2)] \exp(-b_1 Q_1). \quad (15)
\end{aligned}$$

The dispersion component of the 3-body term was damped, as in [15], by taking a product of three 2-body damping functions as follows

$$\begin{aligned}
V_{abc}(\text{disp}) = & C_9 D_3(r_{ab}) D_3(r_{bc}) D(r_{ca}) (r_{ab} r_{bc} r_{ca})^{-3} \\
& \times (1 + 3 \cos \theta_a \cos \theta_b \cos \theta_c), \quad (16)
\end{aligned}$$

D_3 having the same form as expression (10) with independent values for k and β which we will call k_3 and β_3 .

As input data for a least-squares fitting procedure we took D_{3h} geometries and C_{2v} geometries with apical angles of 30° , 90° , and 120° . Bond lengths were chosen at intervals of 0.25 \AA , between lower and upper limits appropriate to each set; these limits were such as to exclude very repulsive regions of the potential and to go sufficiently far into the dissociation regions to obtain effectively the diatomic energies.

The optimum values for the parameters are presented in tables 2 and 3. All energies are in kcal mol^{-1} , and distances in \AA . The units of all parameters are

Table 2. Fitted parameters for 2-body potentials (see text for definition of each parameter); distances in \AA and energies in kcal mol^{-1} . The root-mean-square errors (rms) have been calculated for the number of data points mentioned in the text.

Parameters	Be ₂	Mg ₂	Ca ₂
$V(\text{exch})$			
a_0	9.836 (3) ^a	-3.489 (3)	-4.718 (4)
a_1	-9.021 (3)	1.472 (4)	5.102 (4)
a_2	2.906 (3)	-6.068 (3)	-1.339 (4)
a_3	-2.960 (2)	8.144 (2)	1.074 (3)
α	1.920 (0)	2.230 (0)	1.980 (0)
rms	5.70 (-2)	9.80 (-2)	6.00 (-3)
$V_2(\text{disp})$			
C_6	4.107 (3)	1.041 (4)	3.287 (4)
C_8	4.853 (4)	1.158 (5)	5.543 (5)
C_{10}	2.788 (4)	2.835 (4)	3.617 (5)
β_6	1.540 (0)	4.980 (-1)	7.310 (-1)
β_8	6.010 (-1)	1.989 (0)	2.494 (0)
β_{10}	2.770 (-1)	2.610 (-1)	3.730 (-1)
k_n^b	6.5	7.0	8.0
rms	7.00 (-3)	3.36 (-2)	1.82 (-2)

^a The notation 9.836 (3) means 9.836×10^3 .

^b The same value of k_n was taken for each D_n in the dispersion part of potential (9).

Table 3. Fitted parameters for 3-body potentials (see text for definition of each parameter); distances in \AA and energies in kcal mol^{-1} .

Parameter	Be ₃	Mg ₃	Ca ₃
b_1	2.187 (0) ^a	1.016 (0)	1.402 (0)
b_2	-5.751 (5)	2.692 (3)	-4.710 (4)
b_3	3.537 (5)	-2.193 (3)	3.846 (4)
b_4	-6.242 (4)	2.241 (2)	-7.807 (3)
b_5	-5.296 (4)	2.179 (3)	-9.334 (4)
b_6	3.851 (4)	-1.698 (3)	-1.714 (4)
b_7	-9.112 (3)	3.781 (2)	1.805 (4)
b_8	-7.203 (4)	-3.499 (2)	1.624 (5)
b_9	4.079 (4)	2.062 (2)	-6.781 (4)
b_{10}	-3.601 (3)	-9.744 (1)	7.819 (2)
b_{11}	-1.514 (4)	2.347 (2)	-1.640 (4)
b_{12}	1.032 (4)	-1.574 (2)	-6.108 (3)
b_{13}	-9.708 (2)	4.954 (0)	2.446 (2)
b_{14}	2.999 (2)	1.739 (2)	3.209 (4)
b_{15}	-3.956 (3)	1.663 (1)	-2.233 (3)
b_{16}	5.180 (2)	-7.840 (-1)	4.961 (1)
β_3	4.000 (-1)	1.200 (0)	5.000 (-1)
k_3	1.5	6.0	6.0
C_9^b	4.1585 (3)	2.27756 (4)	2.206014 (5)
rms	4.50 (-1)	3.10 (-1)	1.31 (-1)

^a The notation 2.187 (0) means 2.187×10^0 .

^b The values of C_9 are taken from calculations in [17].

appropriate to these and are obvious from expressions (1)–(6); thus b_1 is kcal mol^{-1} , and b_5 is $\text{kcal mol}^{-1} \text{ \AA}^{-2}$. All the 2-body fittings to the SCF energies were based on 22 points, and the 2-body dispersion terms were based on 28, 26, and 25 point for Be, Mg, and Ca, respectively. The 3-body fitting were based on 58, 47, and 59 points for Be, Mg, and Ca, respectively.

The model potentials and their 2- and 3-body parts are illustrated in figures 1–3. For the dimers the potential curves are very shallow with the depth of the well being only a few kcal/mol. The equilibrium distance increases from Be₂ to Mg₂ to Ca₂. This increase correlates with an increase in the average radius of the atomic valence shell [22]. For the trimers, the potential curves are much deeper than for dimers: more than 10 times for Be and 5–7 times for Mg and Ca. The 3-body forces stabilize the alkaline-earth trimers, and this confirms the importance of introducing the 3-body terms in our model potentials.

To the best of our knowledge, experimental data for the alkaline-earth trimers have not been reported. The quality of the model potential obtained can be checked only by comparison with theoretical calculations. The model potential values of equilibrium geometry (r_0) and binding energy (E_b) for trimers with D_{3h} symmetry and our reference *ab initio* calculations at the MP4 (SDTQ) level are presented in table 4. The agreement is quite satisfactory. We show in table 4 some data from

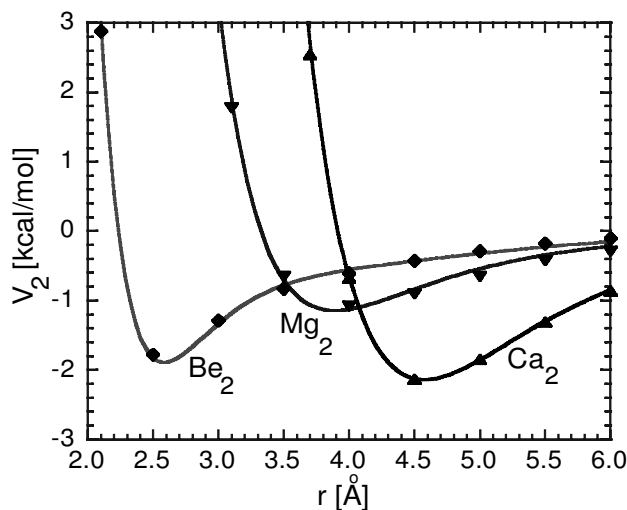


Figure 1. Variation of the 2-body potential V_2 with interatomic distance r in the equilateral (D_{3h}) clusters of Be_2 , Mg_2 , and Ca_2 . The *ab initio* values are given for selected points (symbols).

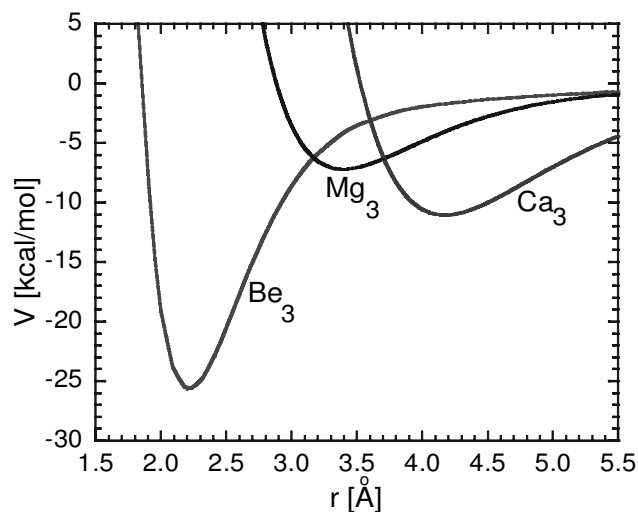


Figure 3. Variation of the total potential V with interatomic distance r in the equilateral (D_{3h}) clusters of Be_3 , Mg_3 , and Ca_3 .

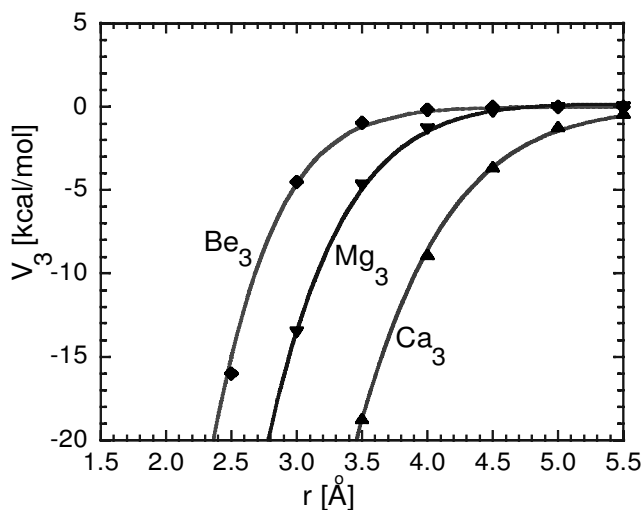


Figure 2. Variation of the 3-body potential V_3 with interatomic distance r in the equilateral (D_{3h}) clusters of Be_3 , Mg_3 , and Ca_3 . The *ab initio* values are given for selected points (symbols).

the best published theoretical studies on the trimers. A comparison with our calculations indicates that the choice of the MP4 (SDTQ) method as a reference *ab initio* approach for fitting parameters is well justified, e.g., the binding energies are reproduced with a chemical precision, about 1 kcal mol^{-1} . A more detailed discussion on the accuracy of our *ab initio* calculations was given in [8].

The equilibrium distances for the dimers are rather large, especially for Mg_2 and Ca_2 , and the addition of one more atom leads to a substantial decrease (see

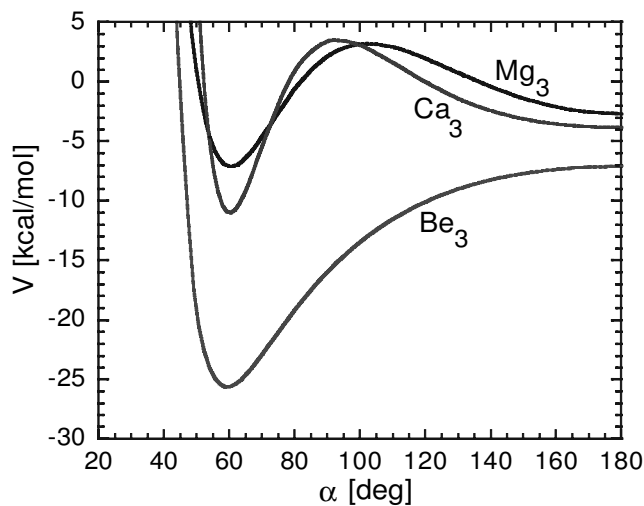


Figure 4. Variation of the total potential V for equilibrium distances and different apical angle α in the isosceles (C_{2v}) clusters of Be_3 , Mg_3 , and Ca_3 .

figure 3). The explanation for this is that the attractive 3-body forces become much larger with a decrease in the atom–atom distances while the 2-body forces undergo only small changes because of the relative flatness of the 2-body potential curves.

The variation of the model potential with the apical angle for the isosceles trimers is shown in figure 4. For non Jahn–Teller–molecules the most stable conformation is expected to be the equilateral triangle, and this is true for all trimers studied. For Be_3 a further increase in α leads to monotonic increase in the energy, whereas for Mg_3 and Ca_3 our model potential reveals the maximum in the vicinity of $\alpha = 100^\circ$.

Table 4. Comparison of model potential values of equilibrium geometries (R_0) and binding energies (E_b) for the trimers (D_{3h} geometries) with the reference *ab initio* calculation (MP4) and some published calculations; distances in Å, energies in kcal mol⁻¹.

	Be ₃		Mg ₃		Ca ₃	
	R_0	E_b	R_0	E_b	R_0	E_b
Model potential	2.21	25.68	3.39	7.21	4.17	11.05
MP4 (SDTQ)	2.24	25.90	3.32	7.12	4.12	11.66
MRCI [23]	2.22	22.4	3.37	6.30		
Best estimations, MP2-R12 [24]	2.20	26.9	3.37	8.00		
CI [25]					3.97	11.53
MRCI [26]					4.16	12.10

As mentioned earlier, to derive a potential function of the type we use up to the 5th order polynomial terms (15), only *ab initio* calculations of the D_{3h} and C_{2v} structures are needed. This potential is also applicable to C_s structures, and would be expected to be a good model, at least for structures not too far from a C_{2v} geometry. However, one cannot guarantee applicability over all space, and far from C_{2v} geometries one might get some unphysical behaviour, such as very deep minima, which would make molecular dynamic simulations invalid. We have checked that our potentials have no unphysical behaviour over a wide range of C_s structures by evaluating them at angles between 15° and 180° at intervals of 15°, and the r_{ab} and r_{ac} distances varied between 1.5 Å and 18.5 Å with steps of 0.5 Å.

3. Conclusion

A general procedure for the construction of *ab initio* many-body model potentials for closed shell (subshell) atom clusters is described and applied to the alkaline-earth clusters. An analysis of the physical contributions to the interaction energy allows one to choose an appropriate analytical form for the potential by separating the model potential into parts each having a clear physical interpretation. The parameters of each part of the model potential can be fitted separately to the corresponding parts of the *ab initio* calculated potential surfaces. The potential surfaces have been calculated using a high level *ab initio* method which includes electron correlation.

The analytical form used in our model potentials is accurate over a broad range of atom–atom distances. So after fitting, these electron correlated *ab initio* model potentials can be utilized in molecular dynamics simulations of metal clusters to study their structural and dynamic properties, in collision dynamics and other physical and chemical applications.

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References

- [1] SCOLES, G. (ed.), 1990, *The Chemical Physics of Atomic and Molecular Clusters* (Amsterdam: North Holland)
- [2] HABERLAND, H. (ed.), 1994, *Clusters in Atoms and Molecules* (Berlin: Springer-Verlag)
- [3] ANDERSEN, H. H. (ed.), 1997, *Proceedings of the Seventh International Symposium on Small Particles and Inorganic Clusters* (Berlin: Springer-Verlag); see also 1997, *Z. Phys. D*, **40**, Nos 1–4.
- [4] *Proceeding of the Eighth International Symposium on Small Particles and Inorganic Clusters*.
- [5] JORTNER, J., 1992, *Z. Phys. D*, **24**, 247.
- [6] KAPLAN, I. G., SANTAMARÍA, R., and NOVARO, O., 1996, *Surfac Rev. Lett.*, **3**, 235.
- [7] KAPLAN, I. G., HERNÁNDEZ-COBOS, J., ORTEGA-BLAKE, I., and NOVARO, O., 1996, *Phys. Rev. A*, **53**, 2493.
- [8] KAPLAN, I. G., ROSZAK, S., and LESZCZYNSKI, J., 2000, *J. Chem. Phys.*, **113**, 6245
- [9] KITTEL, C., 1996, *Introduction to Solid State Physics*, 7th Edn (New York: Wiley).
- [10] KOLOS, W., NIEVES, F., and NOVARO, O., 1976, *Chem. Phys. Lett.*, **41**, 431
- [11] KAPLAN, I. G., 1999, *Intl J. Quantum Chem.*, **74**, 241.
- [12] KAPLAN, I. G., 1999, *Adv. Quantum Chem.*, **31**, 137.

- [13] KAPLAN, I. G., GARZÓN, I. L., SANTAMARÍA, R., VAISBERG, B. S., and NOVARO, O., 1997, *J. molec. Struct. Theochem*, **398–399**, 333.
- [14] COHEN, M. J., and MURRELL, J. N., 1996, *Chem. Phys. Lett.*, **260**, 371.
- [15] HERNÁNDEZ-COBOS, J., KAPLAN, I. G., and MURRELL, J. N., 1997, *Molec. Phys.*, **92**, 63.
- [16] GARZÓN, I. L., KAPLAN, I. G., SANTAMARÍA, R., and NOVARO, O., 1998, *J. chem. Phys.*, **109**, 2176.
- [17] STANDART, J. M., and CERTAIN, P. R., 1985, *J. chem. Phys.*, **83**, 3002.
- [18] FRISCH, J., TRUCKS, G. W., SCHLEGEL, H. B., SCUSERIA, G. E., ROBB, M. A., CHEESEMAN, J. R., ZAKRZEWSKI, V. G., MONTGOMERY, J. A., JR., STRATMANN, R. E., BURANT, J. C., DAPPRICH, S., MILLAM, J. M., DANIELS, A. D., KUDIN, K. N., STRAIN, M. C., FARKAS, O., TOMASI, J., BARONE, V., COSSI, M., CAMMI, R., MENNUCCI, B., POMELLI, C., ADAMO, C., CLIFFORD, OCHTERSKI, J., PETERSON, G. A., AYALA, P. Y., CUI, Q., MOROKUMA, K., MALICK, D. K., RABUCK, A. D., RAGHAVACHARI, K., FORESMAN, J. B., CIOŚŁOWSKI, J., ORTIZ, J. V., STEFANOV, B. B., LUI, G., LIASHENKO, A., PISKORZ, P., KOMAROMI, I., GOMPERTS, R., MARTIN, R. L., FOX, D. J., KEITH, T., AL-LAHAM, M. A., PENG, C. Y., NANAYAKKARA, A., GONZALEZ, C., CHALLACOME, M., GILL, P. M. W., JOHNSON, B., CHEN, W., WONG, M. W., ANDRES, J. L., GONZALEZ, C., HEAD-GORDON, M., REPLOGLE, E. S., and POPLE, J. A., 1998, Gaussian98, Revision A.6 (Pittsburgh, PA: Gaussian, Inc.).
- [19] KRISHNAN, R., BINKLEY, J. S., SEEGER, R., and POPLE, J. A., 1980, *J. chem. Phys.*, **72**, 650.
- [20] KAPLAN, I. G., 1986, *Theory of Molecular Interactions* (Amsterdam: Elsevier).
- [21] MURRELL, J. N., and MOTTRAM, R. E., 1990, *Molec. Phys.*, **69**, 571.
- [22] BUNGE, C. F., BARRIENTOS, J. A., and VIVIER-BUNGE, A., 1993, *At. Data nucl. Data Tables*, **53**, 113.
- [23] LEE, T. J., RENDEL, A. P., and TAYLOR, P. R., 1990, *J. chem. Phys.*, **92**, 489; **93**, 6636.
- [24] KLOPPER, W., and ALMLÖF, J., 1993, *J. chem. Phys.*, **99**, 5167.
- [25] WALCH, S. P., and BAUSCHLICHER, JR., C. W., 1985, *J. chem. Phys.*, **83**, 5735.
- [26] LEE, T. J., RENDELL, A. P., and TAYLOR, P. R., 1992, *Theoret. Chim. Acta*, **83**, 165.