# THE ELECTRONIC STRUCTURE OF SMALL CLUSTERS OF SODIUM

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The electronic structures of small clusters of sodium atoms are calculated using the semi-empirical diatomics-inmolecules method.

## 1. Introduction

Small clusters of metal atoms are of current interest because of their catalytic properties [1]; however, very little is known about the physical or chemical properties of such clusters, or indeed of clusters of even the simplest atoms. This paper is a theoretical study of the electronic properties of sodium atom clusters, for which some experimental data is available on the effects of size and number of atoms on physical properties. The most extensive experimental work on the effect of cluster size on a physical property is that of Leckenby, Robbins et al. [2] who studied the ionization potential of sodium clusters, Na, from n = 3 to n = 12. This work indicates that the ionization potential of these clusters can be approximated by that of a small spherical droplet of bulk metal of the appropriate size. The natural question which arises is whether any other properties of interest can be so treated.

There have been a number of approximate quantum mechanical calculations which give predictions for the ground state energy and geometry of clusters. Baetzold [3] has used extended Hückel and CNDO methods for Ag<sub>n</sub> and Pd<sub>n</sub>, while Companion [4], Ellison [5] and Pickup [6a] have used the diatomics in molecules method for Li<sub>n</sub>. Both of these methods give approximate potential surfaces from which atomization energies and other properties can be computed. Witehead and Grice [6b] have used the DIM method for mixed alkali triatomics, while Janoschek [6c] and von Niessen [6c] have used LCAO MO methods for Li<sub>4</sub>. In addition, Burton [7] and Hoare and Pal [8] have used a simple Lennard-Jones potential to compute total energies. Finally, Johnson et al. [9] have used the SCF- $X_{\alpha}$  method for Li<sub>n</sub> for restricted geometries. The latter are likely to be the most accurate calculations of those mentioned.

In the present paper, we use the diatomics-in-molecules approach (DIM) which for the systems considered herein can be considered an extension of the London, Eyring, Polanyi, Sato (LEPS) valence bond calculations for three atom interactions [10a]. Taylor et al. [10b] have also applied this method to sodium clusters in which the atoms sit on sites in a cubic lattice, in an attempt to study microcrystal growth. This procedure has given good results for many systems, but is also capable of large error. We will discuss this below.

The paper is set out in the following manner: in section 2, general formulae for the DIM energies for small cluster of 4, 5 and 6 atoms are given and the formulae for special geometires are discussed in detail. In section 3, the potential curves for Na<sub>2</sub> are discussed and the results of the DIM calculations for Na<sub>n</sub>, n = 3-6 are presented in section 4. These results are discussed in section 5.

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# 2. DIM formulae

In the DIM method with neglect of interatomic overlap<sup>\*</sup> the input consists of the diatomic potential curves [12]. For the present discussion of the alkalis (and hydrogen) let us assume both the lowest singlet curve  $U^{(0)}(R)$ , and the lowest triplet curve,  $U^{(1)}(R)$ , for a diatomic with its one valence electron in an s-state are known, and are all the information required to understand clusters. We define

$$J = \frac{1}{2} \left[ U^{(0)}(R) + U^{(1)}(R) \right], \qquad (2.1)$$

$$K = \frac{1}{2} \left[ U^{(0)}(R) - U^{(1)}(R) \right].$$
(2.2)

Notice that K is less than zero for the values of R considered herein and that J is usually negative for the important region near the singlet minimum. For  $H_2$ , both of these curves are known exactly and the triplet curve is strongly repulsive near the singlet minimum. For the alkalis, these curves are known less well, but it is certain that the triplet curve is less strongly repulsive than in  $H_2$  so that qualitative differences occur in the two cases.

Given the Coulomb and exchange integrals, J and K, we may write down the appropriate formulae for the small clusters.

### 2.1. Three and four atom clusters

For three atom clusters, the formula for the lowest S = 1/2 states is the LEPS form. The distances between atoms a, b, and c are written  $R_{ab}$ ,  $R_{ac}$ ,  $R_{bc}$ as usual. The collection of these distances will be designated by R. Then

$${}^{3}E_{\pm}^{(1/2)}(R) = J_{ab} + J_{ac} + J_{bc}$$

$$+ \frac{1}{2} [(K - K)^{2} + (K - K)^{2} + (K - K)^{2}]^{1/2}$$
(2.3)

$$\pm \frac{1}{\sqrt{2}} \left[ (\Lambda_{ab} - \Lambda_{ac})^{-+} (\Lambda_{ab} - \Lambda_{bc})^{-+} (\Lambda_{ac} - \Lambda_{bc})^{--} \right]^{--}$$

where

$$J_{ab} \equiv J(R_{ab}), \qquad K_{ab} = K(R_{ab}).$$
 (2.4)

The energy of the S = 3/2 state is given by

$${}^{3}E^{(3/2)}(R) = J_{ab} + J_{ac} + J_{bc} - K_{ab} - K_{ac} - K_{bc}$$
  
$$\equiv U_{ab}^{(1)} + U_{ac}^{(1)} + U_{bc}^{(1)}.$$
 (2.5)

\* This causes an insignificant difference in the calculations; in addition, Steiner et al. [11] have shown that it is necessary to neglect overlap in the DIM method. For the four atom clusters, we have singlet states

$${}^{4}E_{\pm}^{(0)}(R) = \sum_{i>j} (J_{ij}) \pm \frac{1}{\sqrt{2}} \left[ (K_{ac} + K_{bd} - K_{ab} - K_{cd})^{2} (2.6) + (K_{ac} + K_{bd} - K_{ad} - K_{bc})^{2} + (K_{ab} + K_{cd} - K_{ad} - K_{bc})^{2} \right]^{1/2},$$

a quintet state

$${}^{4}E^{(2)}(R) = \sum_{i>j} (J_{ij} - K_{ij}) = \sum_{i>j} (U^{(1)}_{ij}), \qquad (2.7)$$

and three triplet states whose energies are given as the eigenvalues of the following  $3 \times 3$  matrix:

$${}^{4}\mathsf{E}^{(1)}(R) = \mathsf{I}\left(\sum_{i>j} J_{ij}\right) - \begin{bmatrix} K_{ac} + K_{bd} & K_{cd} - K_{ab} & K_{bc} - K_{ad} \\ K_{cd} - K_{ab} & K_{ad} + K_{bc} & K_{bd} - K_{ac} \\ K_{bc} - K_{ad} & K_{bd} - K_{ac} & K_{ab} + K_{cd} \end{bmatrix}$$
(2.8)

For special, symmetric geometries we can simplify these formulae as shown in table 1.

We see that the 4 atom tetrahedral structure has a degenerate singlet state which means that it is unstable with respect to a distortion (Jahn–Teller effect) of e-symmetry. The lowest state of the four atom structure will be either the square or the dispenoidal  $(D_{2h})$  geometry depending on the details of the potential curve.

## 2.2. Five atom clusters

For the five atom clusters there are five DIM states of S = 1/2, four states of S = 3/2 and one state of S = 5/2. For simplicity we will discuss only the S = 1/2states. The energies of these are given as the eigenvalues of the following  $5 \times 5$  matrix.

$$|\mathbf{E}| = \sum_{i>j}^{5} J_{ij} \ \mathbf{1} - \mathbf{K}^{(5)}, \tag{2.9}$$

where the form for K is given in the appendix. For special, symmetric geometries the eigenvalues of K can be found easily and are listed in table 2.

### 2.3. Six atom clusters

For these molecules, there are five DIM states of

Table 1

Gcometry (remarks)	State and energy
3 atom isoceles triangel (apex = c)	${}^{3}E_{+}^{(1'2)} = U_{ab}^{(0)} + \frac{1}{2}U_{ac}^{(1)} + \frac{1}{2}U_{ac}^{(0)}$ ${}^{3}E_{-}^{(1'2)} = U_{ab}^{(1)} + \frac{3}{2}U_{ac}^{(0)} - \frac{1}{2}U_{ac}^{(1)}$
4 atom reg. tetrahedron (all bonds equal)	${}^{4}E_{\pm}^{(0)} = 3[U_{ab}^{(0)} + U_{ab}^{(1)}]$ ${}^{4}E^{(1)} = 4U_{ab}^{(1)} + 2U_{ab}^{(0)}(g=3)$
4 atom distorted tetrahedron ( $C_{3v}$ ) (apex = d)	${}^{4}E_{\pm}^{(0)} = \frac{3}{2} [U_{ab}^{(0)} + U_{ab}^{(1)}] + \frac{3}{2} [U_{ad}^{(0)} + U_{ad}^{(1)}]$ ${}^{4}E_{\pm}^{(1)} = \begin{cases} 3[U_{ab}^{(1)}] + 2U_{ad}^{(0)} + U_{ad}^{(1)} \\ \frac{3}{2} [U_{ab}^{(0)} + U_{ab}^{(1)}] + \frac{5}{2} U_{ad}^{(1)} + \frac{1}{2} U_{ad}^{(0)} (g=2) \end{cases}$
4 atom square (D <sub>4</sub> h), numbered clockwise ( $R_{ab}$ is side and $R_{ac}$ is diagonal of square)	${}^{4}E_{*}^{(0)} = [3U_{ab}^{(0)} + U_{ab}^{(1)}] + 2U_{ac}^{(1)}$ ${}^{4}E_{-}^{(0)} = U_{ab}^{(0)} + 3U_{ab}^{(1)} + 2U_{ac}^{(0)}$ ${}^{4}E^{(1)} = \begin{cases} U_{ab}^{(0)} + U_{ab}^{(1)} + 3U_{ac}^{(1)} + U_{ac}^{(0)} \\ 3U_{ab}^{(1)} + U_{ab}^{(0)} + U_{ac}^{(0)} + U_{ac}^{(1)} (g=2) \end{cases}$
4 atom disphenoidal (D <sub>2d</sub> ), "crossed" diatomics (R <sub>ab</sub> = R <sub>cd</sub> : R <sub>ac</sub> = R <sub>ad</sub> = R <sub>bc</sub> = R <sub>bd</sub> )	${}^{4}E_{+}^{(0)} = 2U_{ab}^{(0)} + 3U_{ac}^{(1)} + U_{ac}^{(0)}$ ${}^{4}E_{-}^{(0)} = 2U_{ab}^{(1)} + U_{ac}^{(1)} + 3U_{ac}^{(0)}$ ${}^{4}E^{(1)} = \begin{cases} 2U_{ab}^{(1)} + 2U_{ac}^{(1)} + 2U_{ac}^{(0)} \\ U_{ab}^{(1)} + U_{ab}^{(0)} + 3U_{ac}^{(1)} + U_{ac}^{(0)} \end{cases}$

Table 2 Five atom clusters; S = 1/2; eigenvalues of K for symmetric configurations

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Rcg. pentagon	$\begin{cases} K_{ab} + K_{ac} \\ (1 = \sqrt{5}) K_{ab} + (1 = \sqrt{5}) K_{ac} \end{cases} (g=2)$
square pyramid (e 15 apex, square is numbered clockwise)	$\begin{cases} 2K_{ab}  (g=2) \\ 2K_{ac} \\ 2K_{ac} + 2K_{ab} - 2K_{ac} \\ 2K_{ac} - 2K_{ab} + 2K_{ac} \end{cases}$
bipyramid ( $D_{3h}$ ; d and e apices)	$\frac{3K_{ab} + K_{de} - K_{ae} - K_{ad}}{(K_{ae} + K_{ad}) \pm (1/\sqrt{2}) \left[(K_{ae} - K_{de})^2 + (K_{ae} - K_{ad})^2 + (K_{ad} - K_{de})^2\right]^{1/2}} (g=2)$
crossed (D <sub>2</sub> d) $c \bullet e - b = a$	$2K_{ac} (g=2)$ $2K_{ab}$ $2K_{ac} + 2K_{ac} - 2K_{ab}$ $2K_{ac} - 2K_{ac} + 2K_{ab}$
$R_{ab} = R_{cd}$ ( $R_{ce} = R_{de} = R_{be} = R_{ae}$ )	

reg. octahedron e e c f	$2K_{ac} + K_{ef}$ $2K_{ab} + K_{ef}  (g=2)$ $4K_{ab} + 2K_{ac} - K_{ef}$ $6K_{ab} - 2K_{ac} - K_{ef}$
reg. hexagon $f \underbrace{ \begin{array}{c} a \\ e \\ d \end{array}}^{a} b \\ c \\ d \end{array} $	$2K_{ab} + K_{ad}  (g=2)$ $3K_{ad}$ $K_{ab} + 3K_{ac} - K_{ad} = [4(K_{ab} - K_{ad})^{2} + 9(K_{ab} - K_{ac})^{2}]^{1/2}$

S = 0, nine of S = 1, five of S = 2 and one of S = 3. The energies of the S = 0 states are given as the eigenvalues of the following  $5 \times 5$  matrix:

$$\mathbf{E} = \sum_{i>j}^{6} J_{ij} \ \mathbf{1} - \mathbf{K}^{(6)},$$

where  $K^{(6)}$  is given in the appendix. The energies for symmetric geometries are given in table 3.

# 3. Potential curve of Na<sub>2</sub>

The two curves used in this study are the lowest singlet and lowest triplet curves of Na<sub>2</sub>. For the structures we are concerned with, we need the potentials most accurately from  $R \approx 2.2$  Å to  $R \approx 5$  Å. The lower portion of the singlet curve has been determined accurately by Zare and co-workers [12] using laser fluorescent techniques and RKR inversion.

The lowest triplet state curve is much more difficult to determine; however, Pritchard and co-workers [13] have determined some of the parameters of the triplet curves for mixed alkali alkali interactions (e.g., NaK, CsNa, etc) in a series of beautiful spin flip experiments. From these curves, which are not too different from one another, we have synthesized a Na<sub>2</sub> triplet curve of the following simple type:

$$U^{(1)}(R) = \left(\frac{10090.}{r^8} - \frac{664.}{r^6}\right) eV, \qquad (r \text{ in Å}). \quad (3.1)$$

The results reported herein are not sensitive to changing the triplet parameters within the bounds of the



Fig. 1 Singlet (<sup>1</sup>E) and triplet (<sup>3</sup>E) potential curves for Na<sub>2</sub>.

mixed curves given by Pritchard. That is, changing the well depth and position of the minimum of the triplet between the smallest the largest values given for the mixed alkalis does not alter the results significantly. We note that the triplet curve is much less steeply repulsive near the minimum of the singlet curve than in the case for H<sub>2</sub> (where, of course, the curves are known with more accuracy). We also note that we are only interested in the triplet curve in the range of internuclear separation from  $\sim 2.75$  Å to  $\sim 4.5$  Å, so we have not included in  $U^{(1)}(R)$  the asymptotic form of Dalgarno and Rudge [13b] and Knox and Rudge [13c]. As Pritchard points out [13a], these forms do not fit all the data known at that time. We emphasize that the important point for our discussion is that the triplet curve is not very repulsive in the region of interest.

Finally, we note that the RKR singlet potential is different from a 6-8 or Morse curve close to the minimum (the RKR being narrower). Using a 6-8 or Morse curve changes the final results somewhat from those reported here.



Fig. 2. Potential curves for special geometires of Na<sub>4</sub>; full line: square; dashed line: tetrahedron; dot-dashed line: perpendicular crossed (disphenoidal) with  $R_{ab} = R_{cd} = 3.1$ Å. The variable, r, is the side length for the square and tetrahedron and is the distance between midpoints for the cross.

### 4. Numerical results

In fig. 2, the lowest energy surface is given for a number of special geometries of four atom clusters. We note that the lowest energy form is the crossed  $(D_{2d})$  geometry, which can be viewed as a distorted tetrahedron. Since the tetrahedral structure will have a two fold degeneracy, the Jahn-Teller theorem requires that the distorted structure be lower in energy. In  $Li_4$  and  $H_4$ , the diatomics in molecules theory gives the square geometry as lowest in energy, in contrast with the present results for Na<sub>1</sub>. However, the two structures are extremely close in energy. In the present case, the square configuration is at a minimum of potential energy with respect to all motions, as is the crossed configuration of lowest energy. This means there are at least two minima in the four atom surface, a complication which may have an effect on the properties of these systems as measured from nozzle beam sources.

The results for Li<sub>4</sub> [4] are not too dissimilar from these for Na<sub>4</sub> in the DIM method. However, in Li<sub>4</sub>, the square configuration is lowest. In the SCF-X<sub> $\alpha$ </sub> results of Johnson for Li<sub>4</sub>, it is found that the spin polarized technique predicts a square to be lowest and the tetrahedral to be almost as low in energy. Since the spin polarized wavefunctions will lower the degeneracy (in the tetrahedral structure) from the  $t^2$  electronic configuration, a portion of the lowering which would be ascribed to Jahn-Teller distortion is taken into account already. The distortion of the tetrahedron has not been investigated as yet by Johnson et al. The SCF-X<sub> $\alpha$ </sub> results also predict that the minimum energy square in Li, will have a near neighbor distance of 3.5 Å whereas the DIM calculation predicts ~2.9 Å. The value in the SCF-X<sub> $\alpha$ </sub> is singular in that it is the largest nearest neighbor distance found by Johnson et al. for the many clusters (up to n = 13) they examined; the value 2.9 Å is much closer to the values for the other clusters calculated by Johnson et al.

We also note that in  $H_4$ , the DIM method gives a total energy for the square configuration which is lower by  $\sim 60$  kcal/mole than the best ab-initio calculation. In fact, the DIM method predicts that the square configuration (at the saddle point of the  $H_2-H_2$  interaction) has lowest total energy [14] -2.193 hartree at r = 2.0 bohr while Conroy and Malli [15] predict -2.152 hartree at 2.2 bohr. Rubinstein and Shavitt [16] give -2.075 hartree at R = 2.47 bohr, and Silver and Stevens [17] give -2.099 hartree at r = 2.4 bohr. Conroy and Malli, and Silver and Stevens claim that their results rule out the square geometry for H<sub>4</sub> and thus the DIM results which give an activation energy near the experimental value (based on the square geometry) would be in error by pprox 60kcal/mole. Whether the same is true for Li<sub>4</sub> and Na4 is not known, of course. It should be pointed out that the DIM results for linear H<sub>4</sub> are in good agreement with the ab initio calculations.

In figs. 3 and 4, the lowest DIM energy surfaces for a number of special geometries for Na<sub>5</sub> and Na<sub>6</sub> are shown. It can be seen that for Na<sub>5</sub>, the DIM method predicts that the square pyramidal and bipyramidal geometries are quite close in energy over the distances considered. For Na<sub>6</sub>, the *eclipsed* equilateral triangles are lower in energy by ~0.1 eV over the octahedral structure, and is the lowest energy structure.

In table 4, we list the total binding energies and atomization energy (neglecting zero point energy) for the most stable structures for the cluster sizes considered. Two trends are indicated: (a) the atomization



Fig. 3. Potential curves for special regular geometries of Nas: full line: regular pentagon; dashed line: square pyramid; dotdashed line: trigonal bipyramid. The variable r is the bond distance between nearest neighbor atoms in each case.



Fig. 4. Potential curves for special regular geometries of Na6: full line: regular octahedron; dashed line: eclipsed equilateral triangles; dot-dashed line: staggered equilateral trianges. The variable, r is the side length for the octahedron, and is the distance between the midpoints of the triangles in other cases.

Table 4

Total binding e	energies and	atomization	energy	for	most	stable
clusters (in cV)	)					

n	E <sub>B</sub> <sup>a)</sup>	E <sub>A</sub> b)	
2	0.70	0.35	
3	0.96	0.32	
4	1.98	0.50	
5	2.33	0.46	
6	3.54	0.59	

a)  $E_B = |E_{most stable} - nE_{atom}|$ . b)  $E_A = E_B/n$ .

energy is increasing with size, and (b) there is oscillation of atomization energy with n, the even numbered clusters being more stable. The value of the standard enthalpy of atomization (at 298 K) of Na4 has been inferred from pVT measurements [18] to be 41.5 kcal/mole. Our value for the energy from the bottom of the potential surface of Na<sub>4</sub> to free atoms is 45.5 kcal/mole. We have not computed the zero point energy, but estimate it to between 1 and 2 kcal/mole, thus bringing our value of  $\Delta E_{0K}$  to ~44 kcal/mole, in reasonably good agreement with the value of Ewing et al.

### 5. Conclusions

The diatomics in molecules method, which was used in this article, has a number of drawbacks as well as a number of good points. It has been shown to give inaccurate numerical results for square H<sub>4</sub> (too much binding); however, the qualitative behavior of the surface near the square configuration is given correctly by DIM. In addition, the quantitative behavior of the surface for linear  $H_4$  is given correctly by DIM. These facts, in addition to the work of Ellison and coworkers [5, 14], have led us to believe that this method is capable of surprising accuracy. The method is very economical in computer time and storage, and thus is capable of mapping out large portions of the potential surface inexpensively.

The numerical results for the sodium clusters indicate that these potential surfaces are extremely complicated with many minima and saddle points. This means that the vibrational structures of the molecules may also be complicated, and that the molecules may

exist in a *few* geometric forms at low temperatures. We intend to study these problems as well as the ionization potentials in a future publication.

The most important result of these calculations is that the closest packed geometires are not necessarily the lowest energy structures for these clusters. If the interaction energy could be taken as a sum of two atom terms which are spherically symmetric (e.g., Lennard-Jones potentials), then closest packed geometries ought to be most stable. The introduction of the spin symmetries in the manner outlined above has led to stabilization for other than most closely pakced geometries. In addition, there are many Jahn-Teller splittings occurring on the potential surface which also give rise to lower symmetry solutions. Whether this result is general for larger clusters is not yet known (however, the icosahedral symmetry predicted [9] for 13 atom clusters would not follow this rule).

## Appendix

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(a) The matrix  $K^{(5)}$  is a symmetric five by five array with matrix elements given by

$$\begin{aligned} \kappa_{11}^{(5)} &= -K_{ab} - K_{cd} + \frac{1}{2}(K_{ac} + K_{ad} + K_{ae} \\ &+ K_{bc} + K_{bd} + K_{be} + K_{ce} + K_{de}) \\ \kappa_{22}^{(5)} &= K_{ab} + K_{cd} + \frac{1}{2}(K_{ae} + K_{be} + K_{ce} \\ &+ K_{de} - K_{bc} - K_{ac} - K_{bd} - K_{ad}) \\ \kappa_{33}^{(5)} &= K_{ab} - K_{cd} + \frac{1}{2}(K_{bc} + K_{ac} + K_{ce} \\ &+ K_{bd} + K_{ad} + K_{de} - K_{be} - K_{ae}) \\ \kappa_{44}^{(5)} &= K_{cd} - K_{ab} + \frac{1}{2}(K_{ac} + K_{ad} + K_{ae} \\ &+ K_{be} + K_{bc} + K_{bd} - K_{ce} - K_{de}) \\ \kappa_{55}^{(5)} &= K_{ab} + K_{cd} \\ \kappa_{12}^{(5)} &= -\frac{1}{2}\sqrt{3}(K_{ac} + K_{bd} - K_{ad} - K_{bc}) \\ \kappa_{13}^{(5)} &= \frac{1}{2}\sqrt{3}(K_{ae} - K_{be}) \\ \kappa_{13}^{(5)} &= \frac{1}{2}\sqrt{3}(K_{ce} - K_{de}) \\ \kappa_{15}^{(5)} &= 0 \end{aligned}$$

$$\begin{aligned} \kappa_{23}^{(5)} &= \frac{1}{2} (K_{de} - K_{ae}) \\ \kappa_{24}^{(5)} &= \frac{1}{2} (K_{be} - K_{ae}) \\ \kappa_{25}^{(5)} &= (1/\sqrt{2}) (K_{ae} + K_{be} - K_{ce} - K_{de}) \\ \kappa_{34}^{(5)} &= \frac{1}{2} (K_{bd} + K_{ac} - K_{bc} - K_{ad}) \\ \kappa_{35}^{(5)} &= (1/\sqrt{2}) (K_{de} - K_{ce} + K_{ac} - K_{bd} - K_{ad} + K_{bc}) \\ \kappa_{45}^{(5)} &= (1/\sqrt{2}) (K_{ae} - K_{be} + K_{bd} - K_{ac} - K_{ad} + K_{bc}) . \end{aligned}$$

(b) The matrix  $K^{(6)}$  is a symmetric five by five array with

$$\begin{aligned} \kappa_{11}^{(6)} &= \kappa_{11}^{(5)} - K_{cf} + \frac{1}{2}(K_{af} + K_{bf} + K_{cf} + K_{df}) \\ \kappa_{22}^{(6)} &= \kappa_{11}^{(5)} - K_{cf} + \frac{1}{2}(K_{af} + K_{bf} + K_{cf} + K_{df}) \\ \kappa_{33}^{(6)} &= \kappa_{33}^{(5)} + K_{cf} + \frac{1}{2}(K_{cf} + K_{df} - K_{af} - K_{bf}) \\ \kappa_{44}^{(6)} &= \kappa_{44}^{(5)} + K_{cf} + \frac{1}{2}(K_{af} + K_{bf} - K_{cf} - K_{df}) \\ \kappa_{44}^{(6)} &= \kappa_{44}^{(5)} + K_{cf} + \frac{1}{2}(K_{af} + K_{bf} - K_{cf} - K_{df}) \\ \kappa_{55}^{(6)} &= \kappa_{55}^{(5)} + K_{ef} \\ \kappa_{12}^{(6)} &= \kappa_{12}^{(5)} \\ \kappa_{13}^{(6)} &= \kappa_{12}^{(5)} + \frac{1}{2}\sqrt{3} (K_{bf} - K_{af}) \\ \kappa_{14}^{(6)} &= \kappa_{14}^{(5)} + \frac{1}{2}\sqrt{3} (K_{df} - K_{cf}) \\ \kappa_{16}^{(6)} &= 0 \\ \kappa_{23}^{(6)} &= \kappa_{25}^{(5)} + \frac{1}{2}(K_{af} - K_{bf}) \\ \kappa_{24}^{(6)} &= \kappa_{25}^{(5)} + (1/\sqrt{2}) (K_{cf} + K_{df} - K_{af} - K_{bf}) \\ \kappa_{34}^{(6)} &= \kappa_{34}^{(5)} + (1/\sqrt{2}) (K_{af} - K_{cf}) \\ \kappa_{35}^{(6)} &= \kappa_{35}^{(5)} + (1/\sqrt{2}) (K_{af} - K_{cf}) \\ \kappa_{45}^{(6)} &= \kappa_{45}^{(5)} + (1/\sqrt{2}) (K_{af} - K_{bf}). \end{aligned}$$

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