

Calculation of Puckered Rings with Analytical Gradients

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Puckering coordinates are useful for the description of nonplanar N -membered rings. They can also be applied when optimizing the geometry of a puckered ring molecule. For this purpose, analytical gradients have to be extended to puckering coordinates, which can easily be done by calculating the corresponding elements of the Wilson **B** matrix. Formulas for setting up analytical gradients in terms of puckering coordinates are given, and their use in geometry optimizations of puckered rings is discussed.

1. Introduction

The investigation of puckered rings with *ab initio* methods has been limited to small rings and high-symmetry forms of medium-sized rings.¹ This has to do with the fact that geometry optimizations of puckered N -membered rings lead to a number of problems. For example, there is no unique way of selecting $3N - 6$ bond lengths and bond angles out of a total number of $3N$ bond lengths, bond angles, and dihedral angles. There are always six parameters, e.g., three bond angles and three dihedral angles, that depend on the $3N - 6$ parameters selected. If the starting values for the latter are not carefully determined, abnormal values for the dependent parameters and, thereby, a bad starting energy will result. A way to circumvent this problem is to choose linear combinations of internal coordinates. For example, it has been suggested to use symmetry coordinates to describe the out-of-plane deviations of a puckered N -membered ring.^{3,4} But even in this case a number of problems remain. It is difficult to specify low-symmetry forms of larger rings and to describe their relationship in terms of internal coordinates such as dihedral angles. A simple answer to the question of whether two conformers are closely related or separated by a large distance in conformational space cannot be given if just bond lengths, bond angles, dihedral angles, or linear combinations of bond lengths and bond angles are used as internal coordinates.

Another problem has to do with the initial guess for the Hesse matrix **H**. Normally, one assumes that **H** is concentrated on the diagonal and that a set of standard force constants approximates the diagonal elements reasonably. Neither assumption is valid in the case of puckered rings. The diagonal elements of **H** significantly differ from standard force constants. Furthermore, there is strong coupling between internal coordinates of a puckered ring leading to nondiagonal elements of **H** considerably different from zero. Both the initial guess for geometry and Hesse matrix and the coupling between the internal coordinates can lead to convergence problems that make the geometry optimization of a puckered N -membered ring rather costly.

Most of the problems described above will be avoided if the geometry of a puckered N -membered ring is described with the help of the ring-puckering coordinates first suggested by Cremer and Pople.² For an N -membered ring, there are $N - 3$ puckering coordinates that describe the conformation of a nonplanar ring in a unique way.³⁻⁷ The puckering coordinates span the conformational space of a puckered ring which is a subspace of the total $3N - 6$ dimensional configuration space.⁸⁻¹⁰ Conformational

changes of the ring such as pseudorotation or ring inversion can easily be investigated within that subspace by utilizing the puckering coordinates.^{3,5,6} This, however, is not possible when using the N dihedral angles of the ring.¹¹

Various extensions of the concept of the ring-puckering coordinates have been given, e.g., to describe the position of a ring substituent in a unique way,^{8,12} to calculate the standard deviation of experimentally determined puckering coordinates^{13,14} or to facilitate a comparison of puckering coordinates obtained for different ring molecules.¹⁵⁻¹⁸

The concept of the ring puckering coordinates is widely used among crystallographers. Computer programs have been developed that calculate puckering coordinates from X-ray data.¹⁹ However, in *ab initio* theory the advantages of the puckering coordinates are still not fully exploited. This has partly to do with the fact that the puckering coordinates are not well-understood and partly with the fact that so far no generally applicable procedure for the use of puckering coordinates in geometry optimizations has been given. Also, no generally applicable program that calculates Cartesian coordinates from puckering coordinates has been published so far. The aim of this work is to fill this gap and to demonstrate how puckering coordinates can be used in geometry optimizations with analytical gradients.

We will proceed in the following sections by first reviewing the concept of the ring-puckering coordinates briefly. Then, we will present formulas to calculate Cartesian coordinates from puckering coordinates. Finally, we will show how puckering coordinates can be used in geometry optimizations based on analytical gradients.

2. Conformational Space of Acyclic and Cyclic Molecules

To assess the conformational flexibility of a molecule, very often it suffices to analyze the molecular energy as a function of a few internal coordinates, in particular the dihedral angles. For example the conformational behavior of *n*-butane can fully be described by developing the molecular energy as a function of the dihedral angle τ (CCCC) (Figure 1). Changes in the energy that arise from a coupling of the dihedral angle τ with the other internal parameters of *n*-butane can be considered as second-order effects that are neglected in a first approximation to the conformational potential of *n*-butane. Hence, the conformational subspace of *n*-butane possesses the dimension one.²⁰

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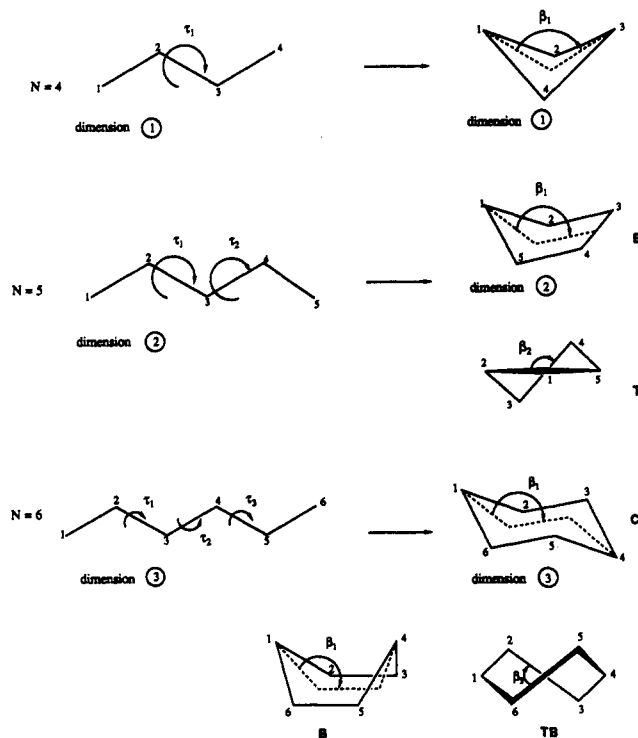


Figure 1. Conformational parameters of the four-, five-, and six-heavy-atom molecules *n*-butane, cyclobutane, *n*-pentane, and cyclopentane. The dimension of the conformational subspace is given for each system.

Similarly, conformational changes of cyclobutane, the cyclic analogue of *n*-butane, can be described within a one-dimensional conformational subspace of the $(3N - 6)$ -dimensional configuration space. The internal parameter, appropriate to describe puckering of a four-membered ring such as cyclobutane, is the folding angle β_1 between the planes C2C1C4 and C2C3C4 (see Figure 1). A change from $\beta < 180$ to $\beta > 180$ indicates inversion of the puckered four-membered ring. If $\beta = 180^\circ$, the four-membered ring will be planar.²¹

In the case of an acyclic five-heavy-atom system such as *n*-pentane, two dihedral angles, $\tau(\text{C1C2C3C4})$ and $\tau(\text{C2C3C4C5})$, suffice to determine the conformation of the molecule. Accordingly, the conformational space is two-dimensional.

If *n*-pentane closes to form cyclopentane, an envelope (E) form or a twist (T) form may result. Puckering of the E form can be described by a folding angle β_1 , puckering of the twist form by a twisting angle β_2 (Figure 1). Again, only two parameters are necessary to assess the conformation of the two five-membered ring forms.

One might argue that there is an infinite number of puckered five-membered ring forms and, therefore, an infinite number of parameters is needed to describe their conformation. However, all these ring forms can be constructed from E and T forms. E and T form are the two basis conformations of the five-membered ring. Any other conformer can be viewed as a linear combination of basis conformations (LCBC) within the two-dimensional conformational space of a five-membered ring.⁸

For six-heavy-atom systems such as *n*-hexane or cyclohexane, three internal parameters suffice to describe any conformer or any conformational change. These are identical with three dihedral angles in the case of an acyclic linear six-heavy-atom system. For a six-membered ring, there are three basis conformations, namely, the chair (C), the boat (B), and the twist-boat (TB) form (see Figure 1). The puckering of each of these three basis conformations is determined by just one folding or twisting angle. Again, any other conformer of a puckered six-membered ring can be constructed as LCBC.⁸

In general, the conformational subspace of an *N*-membered ring possesses the same dimension as that of the corresponding acyclic linear *N*-heavy-atom molecule, namely, $N - 3$. This implies that there exist $N - 3$ basis conformations both for the acyclic and the cyclic system and that any conformer of the *N*-heavy-atom molecule can be described in terms of the $N - 3$ basis conformations.

The $N - 3$ internal coordinates that characterize the basis conformations of a puckered *N*-membered ring are difficult to obtain from folding or twisting angles. There is no general way of defining them for large rings with low symmetry. Also, dihedral angles are not useful since they cannot be reduced from *N* to $N - 3$ in a unique way. Therefore, a different approach has to be taken that is outlined in the next section.

3. Definition of a Reference System: The Mean Plane

A molecular property can be best described with the help of an appropriate reference property of a reference molecule. The obvious thing to do in case of a puckered *N*-membered ring is to define the corresponding planar ring as a suitable reference system. The geometry of the planar *N*-membered ring is fully determined by $2N - 3$ internal coordinates, for example, *N* bond lengths and $N - 3$ bond angles. There remain just $N - 3$ internal coordinates that measure the out-of-plane deviations that lead from the planar reference ring to the puckered ring.

The problem mentioned in the Introduction, namely, the difficulty of selecting $3N - 6$ internal coordinates out of the $3N$ bond lengths, bond angles, and dihedral angles of a nonplanar *N*-membered ring, is reduced to the problem of finding $N - 3$ conformational coordinates out of *N* out-of-plane displacements of a puckered *N*-membered ring. This problem is solved by placing the planar reference ring into the *x,y* plane of a Cartesian coordinate system. To keep the planar ring in the *x,y* plane, a movement of the ring out of the plane either by translation or rotation has to be suppressed.

The out-of-plane deviations of the puckered *N*-membered ring are measured by the *z* coordinates of the ring atoms. The *z* coordinates may indicate an overall movement of the ring or an internal deformation of the ring leading to a puckered form. In Figure 2, this is illustrated for the case of a planar five-membered ring. Translation of the planar reference ring along the *z*-axis is given by eq 1, where $j = 1, N$ and q_0 is a constant that measures

$$z_j = q_0 \quad (1)$$

the length of the translational shift. Overall rotations of the planar ring either around the *x* or the *y* axis are described by eq 2 and 3, with $\alpha_j = 2\pi(j - 1)/N$ (in Figure 2, $N = 5$) and q_1 being a

$$z_j = q_1 \cos \alpha_j \quad (2)$$

$$z_j = q_1 \sin \alpha_j \quad (3)$$

constant describing the degree of overall rotation of the ring.

Translation and overall rotations of the planar reference ring either around the *x* or the *y* axis are suppressed by imposing eqs 4–6 on the out-of-plane deviations z_j .² If (4)–(6) are fulfilled,

$$\sum_{j=1}^N z_j = 0 \quad (4)$$

$$\sum_{j=1}^N z_j \cos \alpha_j = 0 \quad (5)$$

$$\sum_{j=1}^N z_j \sin \alpha_j = 0 \quad (6)$$

the planar ring will be forced to remain in the *x,y* plane. Any set of out-of-plane displacements z_j that describes the deviation of a puckered ring from the planar reference ring must be of the form (7) or (8) to fulfill eqs 4–6 with *m* taking special integer

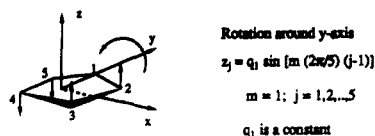
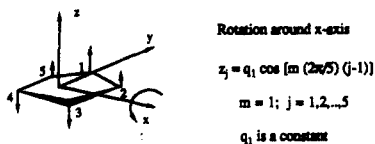
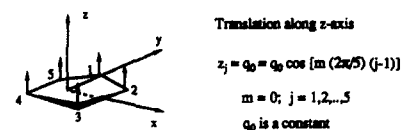
$$z_j = q_m \cos(m\alpha_j) \quad (7)$$

$$z_j = q_m \sin(m\alpha_j) \quad (8)$$

(20) Throughout this work only the heavy-atom framework is considered.

(21) Alternatively, the complementary angle $\beta' = 180 - \beta$ may be used. In this way, the folding angle becomes 0° for the planar form.

Translation and Rotation of the Ring

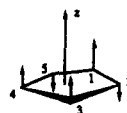


Internal Deformation (Puckering) of the Ring

$$m = 5 \text{ corresponds to } m = 0$$

$$m = 4 \text{ corresponds to } m = 1$$

$$m = 3 \text{ corresponds to } m = 2$$

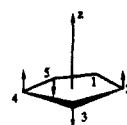


C_2 Deformation \rightarrow Envelope Form

$$z_j = q_2 \cos [m (2\pi/5) (j-1)]$$

$$m = 2; j = 1, 2, \dots, 5$$

q_2 is a constant



C_2 Deformation \rightarrow Twist Form

$$z_j = q_2 \sin [m (2\pi/5) (j-1)]$$

$$m = 2; j = 1, 2, \dots, 5$$

q_2 is a constant

Figure 2. Possible out-of-plane displacements of a planar five-membered ring. See text.

values and q_m being a constant that measures the movement (internal or external) of the N -membered ring. In other words, the mean value of the z_j coordinates of any nonplanar ring conformer has to vanish. This is the reason why the x, y plane is called the mean plane.²

Figure 2 shows that for $m = 2$ and $N = 5$ eq 7 leads to the E and eq 8 to the T form of the five-membered ring. For $m = 3$, the same out-of-plane distortions as for $m = 2$ are obtained. For $m = 4$, eqs 2 and 3 (rotation around the x or y axis) are reproduced, and for $m = 5$ eq 1 (translation along the z axis). Hence, only $m = 2$ leads to a unique internal distortion of the five-membered ring that is in line with eqs 4–6:

$$z_j = q_2 \cos (2\alpha_j) \quad j = 1, 5 \quad (9)$$

$$z_j = q_2 \sin (2\alpha_j) \quad j = 1, 5 \quad (10)$$

An N -membered planar ring possesses just N unique sets of out-of-plane displacements that are given by eqs 7 and 8 with $m = 0, 1, 2, \dots, (N-1)/2$ for N being odd and $m = 0, 1, 2, \dots, N/2$ for N being even. For $m = 0$ overall translation ((7) leads to (1), and (8) describes a zero translation) and for $m = 1$ overall rotation of the planar N -membered ring ((7) leads to (2), (8) to (3)) are described. For $m = 2, \dots, (N-1)/2$ or $m = 2, \dots, N/2$, the $N-3$ genuine basis conformations of the puckered N -membered ring result.

If N is odd, all basis conformations of the N -membered ring will appear in pairs where each pair is characterized by the value of m . The first basis conformation in the pair is defined by eq 7, the second by eq 8. The two basis conformations are related in the same way as the two overall rotations given for $m = 1$, i.e., a phase shift of 90° transforms one form into the other. Therefore, one can speak of a pair of basis conformations connected by an internal "rotation" of the puckering mode of the ring. However, this internal "rotation" does not lead to an overall angular momentum, and therefore the term pseudorotation has been coined.²² Hence, for an odd-membered ring each $m = 2, \dots, (N-1)/2$, defines a pseudorotational pair of basis conformations, the z_j coordinates of which are given by eq 11, with $q_m > 0$ and $0 \leq$

$$z_j = q_m \cos [\phi_m + m\alpha_j] \quad (11)$$

$\phi_m \leq 2\pi$. In eq 11, the two basis conformations connected with the m th pseudorotational mode of an N -membered ring are specified by setting ϕ_m to 0 or 90° rather than using a separate equation for each basis conformation such as eqs 7 and 8.

Equation 11 leads to the out-of-plane displacements z_j of any conformer located in the two-dimensional pseudorotational subspace m of the total conformational space of the puckered N -membered ring. This is done by fixing the values of q_m and ϕ_m . From the derivation given above, it becomes clear that q_m determines the degree of puckering (maximal out-of-plane deviation) and ϕ_m the mode of puckering (phase shift) of any conformer in the m th pseudorotational subspace. Since q_m is a distance and ϕ_m an angle, $\{q_m, \phi_m\}$ represent a set of hypercylindrical coordinates.²

There exist $(N-3)/2$ pairs of basis conformations and, hence, $(N-3)/2$ pseudorotational subspaces for an odd-membered ring.

If N is even, there will be $(N-4)/2$ pseudorotational pairs of basis conformations defined by $m = 2, \dots, (N-2)/2$. In addition, there is a single basis conformation with $m = N/2$. For this value of m , eq 7 leads to (12), while eq 8 does not change the z_j coordinates of the planar ring. Equation 12 describes the crown

$$z_j = q_{N/2} \cos [\pi(j-1)] = q_{N/2} (-1)^{j-1} \quad (12)$$

or all-chair form of an even-membered ring. It can be viewed as the internal counterpart of the overall translation of the planar reference ring given for $m = 0$ (see eq 1). Hence even-membered rings differ from odd-membered rings insofar as they possess, besides $(N-4)/2$ pairs of pseudorotational basis conformations, a single basis conformation that is specified by the degree of puckering $q_{N/2}$. The amplitude $q_{N/2}$ that can be larger or smaller than zero, spans a one-dimensional inversion subspace of puckered even-membered rings.⁸

The out-of-plane displacements z_j of any puckered N -membered ring are determined by $N-3$ puckering coordinates $\{q_m, \phi_m\}$. It is useful to normalize the z_j coordinates according to eq 13,² in

$$\sum_j z_j^2 = \sum_m q_m^2 = Q^2 \quad (13)$$

which Q defines the total puckering amplitude of the N -membered ring. With (13), the equations for the calculation of the z_j coordinates are given by eqs 14 and 15. These coordinates fulfill

$$z_j = (2/N)^{1/2} \sum_{m=2}^{(N-1)/2} q_m \cos [\phi_m + m\alpha_j] \quad (N \text{ odd}) \quad (14)$$

$$z_j = (2/N)^{1/2} \sum_{m=2}^{(N/2)-1} q_m \cos [\phi_m + m\alpha_j] + (1/N) q_{N/2} (-1)^{j-1} \quad (N \text{ even}) \quad (15)$$

equations 4–6, which keep the planar reference ring in the mean plane.

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4. Advantages of the Ring Puckering Coordinates

There are a number of advantages that arise from the use of puckering coordinates in the description of puckered N -membered rings.

1. The ring puckering coordinates are uniquely defined. They do not depend on the size or the symmetry of the N -membered ring.²

2. Ring puckering coordinates can easily be calculated once the Cartesian coordinates of an N -membered ring are known.^{2,19}

3. On the other hand, the Cartesian coordinates of any N -membered ring can easily be derived from its $N - 3$ puckering coordinates and additional $2N - 3$ internal coordinates that describe the planar reference ring.

4. Use of the puckering coordinates allows calculation of the ring geometry in a very economic way utilizing analytical gradients.

5. The puckering coordinates allow to specify the basis conformations of an N -membered ring and to span the conformational subspace of the total $3N - 6$ dimensional configuration space.⁸

6. The puckering coordinates are essential for a quantitative analysis of ring conformations and conformational changes in terms of basis conformations and elementary conformational processes.²⁻⁷

7. The puckering coordinates are a result of the choice of the reference conformation and the reference plane. A corollary of this choice is that the reference plane, the mean plane, is invariant for any conformational processes of any N -membered ring form described in terms of the puckering coordinates (see Appendix for proof).

8. The puckering coordinates can be used for describing the conformational potential of a puckered ring.^{3,5,6}

9. With the help of the mean plane the positions of the ring substituents can be determined in a unique way.^{8,12}

10. The concept of the puckering coordinates provides a basis to analyze coupled internal rotations in acyclic linear molecules.²³

Despite these advantages, the concept of ring puckering coordinates has been criticized.^{25,26} It has been claimed that the puckering coordinates are not appropriate to describe conformational processes since the reference plane chosen for their definition is not invariant under conformational processes. If this would be the case, the whole concept of the puckering coordinates would be erroneous and useless. Therefore, we give a proof in the Appendix that shows that the reference plane is invariant under any conformational process and that claims suggesting the opposite are unjustified.

While most of the advantages listed above have been documented before, a description of a program that calculates Cartesian coordinates from puckering coordinates and that is the prerequisite for using puckering coordinates in geometry optimizations with analytical gradients has not been given so far. Therefore, such a program is described in the next section.

5. Calculation of Cartesian Coordinates from Puckering Coordinates

It is easy to calculate the Cartesian coordinates of any puckered N -membered ring once its $N - 3$ puckering coordinates, $N - 3$ bond angles, and N bond lengths have been specified. The calculation comprises the following steps: 1. Calculation of the z_j coordinates. 2. Projection of N bond lengths and $N - 3$ bond angles into the plane of the planar reference ring. 3. Partitioning of the planar ring into three segments. 4. Calculation of the x, y coordinates of the segments. 5. Calculation of the x_j, y_j coordinates of the planar ring by combining its segments.

Step 1 implies that either eq 14 for odd-membered rings or eq 15 for even-membered rings is used. Once the z_j coordinates are

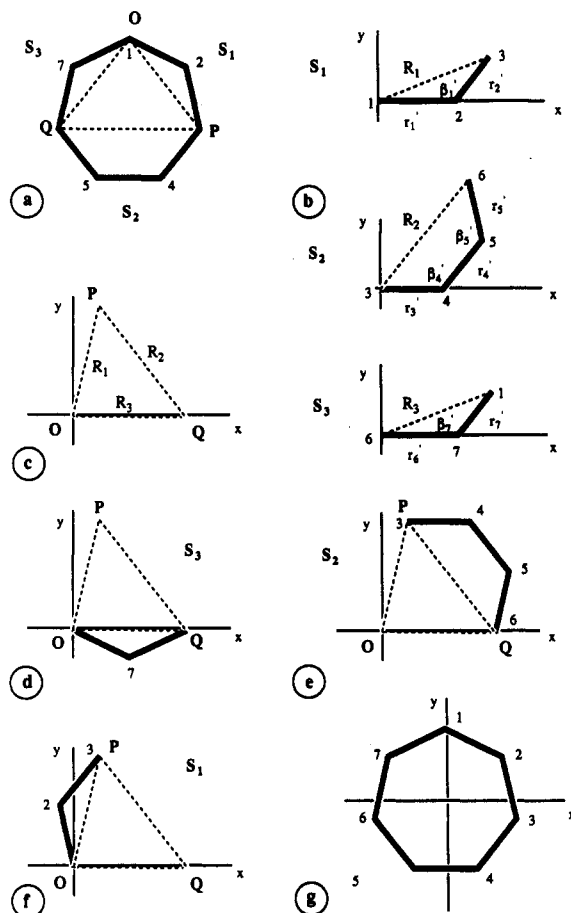


Figure 3. Calculation of the coordinates of a planar seven-membered ring. (a) Partitioning of the ring into three segments S_1, S_2, S_3 by inscribing the triangle OPQ into the ring. (b) Calculation of the x, y coordinates for each segment. (c) Calculation of the x, y coordinates for the triangle OPQ . (d) Orienting segment S_3 . (e) Orienting segment S_2 . (f) Orienting segment S_1 . (g) Orienting the whole ring.

TABLE I: Partitioning of a Planar Ring into Segments $S_1, S_2,$ and S_3 ^a

N	no. of atoms in			no. of bond lengths r' in			no. of bond angles β' in		
	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
5	3	2	3	2	1	2	1	0	1
6	3	3	3	2	2	2	1	1	1
7	3	4	3	2	3	2	1	2	1
8	4	3	4	3	2	3	2	1	2
9	4	4	4	3	3	3	2	2	2
10	4	5	4	3	4	3	2	3	2
11	5	4	5	4	3	4	3	2	3
12	5	5	5	4	4	4	3	3	3

^a N denotes the size of the ring; the number of atoms for S_1, S_2, S_3 is $N + 3$, the number of bond lengths and bond angles in S_1, S_2, S_3 is $2N - 3$.

known, the bond lengths r' and bond angles β' of the planar reference ring can be calculated by projecting N bond lengths r and $N - 3$ bond angles β of the puckered ring into the mean plane:

$$r_{ij}' = [r_{ij}^2 - (z_j - z_i)^2]^{1/2} \quad (16)$$

$$\cos \beta_{ijk}' = [(z_k - z_i)^2 - (z_j - z_i)^2 - (z_k - z_j)^2 + 2r_{ij}'r_{jk}' \cos \beta_{ijk}] / 2r_{ij}'r_{jk}' \quad (17)$$

N projected bond lengths r' and $N - 3$ projected bond angles β' suffice to determine the x_j, y_j coordinates of the planar ring.

For this purpose, the planar reference ring is partitioned into three segments by inscribing into the ring the triangle OPQ (see Figure 3). O is identical with atom 1, and P and Q are determined by the length of the segment. It is convenient to fix the length

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of the segments as shown in Table I and Figure 3a. In this way, error progression due to coupling of the ring parameters is kept at a minimum. In particular, the three unknown internal ring angles that depend on the $2N - 3$ bond lengths and bond angles already fixed will be equally distributed over the ring.

The x , y coordinates of the atoms of each segment can be calculated from the r' and β' values. It is convenient to place the terminal atom with the lowest sequence number k at the origin, atom $k + 1$ on the positive x axis, and atom $k + 2$ in the first quadrant of the x , y coordinate system (Figure 3b).

In the next step, the coordinates of the triangle OPQ are determined by using the distances R_1 , R_2 , R_3 between the terminal atoms of each segment (Figure 3c). The origin is chosen as the position of O and Q is placed on the positive x axis. The remaining coordinates of the triangle OPQ are calculated with the help of R_1 , R_2 , and R_3 . In the following step, segment 3 is rotated in a way that its last atom coincides with Q keeping its first point at the origin (Figure 3d). Then, the last atom of segment 2 is shifted in the x , y plane until it coincides with Q. Rotation at Q brings segment 2 in a position, in which its first point coincides with P (Figure 3e). In the last step, segment 1 is shifted and rotated in the x , y plane until its last point coincides with P (Figure 3f). In this way all coordinates of the planar ring are determined. Eventually, a coordinate transformation that leads to the geometrical centre as the origin of the coordinate system and atom 1 on the positive y axis yields the final set of Cartesian coordinates (Figure 3g).

The procedure outlined can be applied to any N -membered ring with or without symmetry. A computer program has been written that uses this procedure to calculate the Cartesian coordinates of the ring atoms and the substituent atoms. To be compatible with other coordinate programs the input is arranged according to the z matrix formalism most ab initio programs use. Beside the z matrix input, N and the puckering coordinates have to be given.

6. Geometry Calculation of Puckered Rings with Analytical Gradients

Analytical energy gradients are available for many ab initio methods. Normally, the analytical gradients are formed with regard to the Cartesian coordinates $\mathbf{u} = (x, y, z)$ of the atoms of an molecule. The analytical calculation of forces $\boldsymbol{\eta}$ with regard to the internal coordinates ξ (bond lengths, bond angles, and dihedral angles) is done with the Wilson \mathbf{B} matrix that relates an infinitesimal shift of the internal coordinates to a corresponding change in the Cartesian coordinates.^{27,28}

$$d\xi = \mathbf{B} d\mathbf{u} \quad (18)$$

The matrix \mathbf{B} is rectangular and has the elements

$$B_{st} = \partial\xi_s / \partial u_t \quad (19)$$

with $s = 1, \dots, 3N - 6$, and $t = 1, \dots, 3N$. The relationship between Cartesian forces \mathbf{f} and internal forces $\boldsymbol{\eta}$ is given by

$$\boldsymbol{\eta} = (\mathbf{B}^+)^{-1} \mathbf{f} \quad (20)$$

with

$$(\mathbf{B}^+)^{-1} = (\mathbf{BMB}^+)^{-1} \mathbf{B} \mathbf{M}$$

and \mathbf{M} being an auxiliary matrix.

To extend available gradient algorithms to the use of puckering coordinates, the derivatives of $\{q_m, \phi_m\}$ with regard to the Cartesian coordinates have to be calculated for the corresponding \mathbf{B} matrix elements (eq 19).

Since q_m and ϕ_m depend only on z_j , their derivatives with regard to x_j and y_j are zero. It suffices to find $\partial q_m / \partial z_j$ and $\partial \phi_m / \partial z_j$. For this purpose, the puckering coordinates are given as a function of z_j :

$$q_m \cos \phi_m = (2/N)^{1/2} \sum_{j=1}^N z_j \cos \alpha_j = a \quad (21)$$

$$q_m \sin \phi_m = -(2/N)^{1/2} \sum_{j=1}^N z_j \sin \alpha_j = b \quad (22)$$

with $\alpha_j = m(2\pi/N)(j - 1)$ and $m = 2, \dots, (N - 1)/2$ for N being odd and $m = 2, \dots, (N - 2)/2$ for N being even. In the case of even-membered rings, an additional equation is needed for the puckering amplitude of the crown form:

$$q_{N/2} = (1/N)^{1/2} \sum_{j=1}^N z_j \cos[\pi(j - 1)] \quad (23)$$

To separate coordinates q_m and ϕ_m , eqs 21 and 22 are combined:

$$q_m^2 [\cos^2 \phi_m + \sin^2 \phi_m] = a^2 + b^2 \quad (24)$$

With eqs 21, 22, and 24, q_m and ϕ_m can be given as a function of z_j :

$$q_m = (a^2 + b^2)^{1/2} \quad (25)$$

$$\phi_m = \arctan(b/a) \quad (26)$$

Differentiation with regard to z_j leads to

$$\partial q_m / \partial z_j = (a^2 + b^2)^{-1/2} (a \partial a / \partial z_j + b \partial b / \partial z_j) \quad (27)$$

and with

$$\partial a / \partial z_j = (2/N)^{1/2} \partial(z_j \cos \alpha_j + \sum_{i \neq j} z_i \cos \alpha_i) / \partial z_j = (2/N)^{1/2} \cos \alpha_j \quad (28)$$

$$\partial b / \partial z_j = -(2/N)^{1/2} \sin \alpha_j \quad (29)$$

to eq 30:

$$\partial q_m / \partial z_j = (1/q_m)(2/N)^{1/2} [a \cos \alpha_j - b \sin \alpha_j] = (2/N)^{1/2} [\cos \phi_m \cos \alpha_j - \sin \phi_m \sin \alpha_j] \quad (30)$$

For $m = N/2$, the partial derivative simplifies to

$$\partial q_{N/2} / \partial z_j = (1/N)^{1/2} (-1)^{j-1} \quad (31)$$

Similarly, one obtains for $\partial \phi_m / \partial z_j$, eq 32:

$$\begin{aligned} \partial \phi_m / \partial z_j &= \partial[\arctan(b/a)] / \partial z_j = [1 + (b/a)^2]^{-1} \partial(b/a) / \partial z_j = [1 + (b/a)^2]^{-1} (1/a^2) (a \partial b / \partial z_j - b \partial a / \partial z_j) \\ &= (1/q_m)(2/N)^{1/2} [\sin \phi_m \cos \alpha_j - \cos \phi_m \sin \alpha_j] \end{aligned} \quad (32)$$

Equation 32 reveals that for $q = 0$ the partial derivative $\partial \phi_m / \partial z_j$ is no longer defined. This is a consequence of the fact that ϕ_m is not specified for the planar ring.

With (30)–(32) all derivatives of the puckering coordinates are determined, and the calculation of internal forces for puckered rings with the aid of eq 20 is straightforward.

A computer program has been written that calculates analytical gradients for puckering coordinates. The gradient has been tested by comparison with the numerically determined gradient. For geometry optimizations of puckered rings it is convenient to use suitable starting values for the internal forces. Test calculations give

$$f_q = 0.64 \text{ hartree/bohr}^2 \quad f_\phi = 0.23 \text{ hartree/rad}^2$$

The program has been implemented in the ab initio package COLOGNE²⁹ and applied for nonplanar N -membered rings up to $N = 10$.

In Table II, HF/STO-3G energies and geometries for the four basis conformations of cycloheptane, namely, boat (B), twist boat (TB), chair (C), and twist chair (TC) form (Figure 4), are given.³⁰ The basis conformations possess either C_1 or C_2 symmetry, and therefore only 29 and 28 internal coordinates of cycloheptane have

(27) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(28) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.

(29) Gauss, J.; Kraka, E.; Reichel, F.; Cremer, D., Universität Köln, 1988.

(30) Complete sets of optimized parameters can be obtained from the author.

TABLE II: Energies and Optimized Geometries of the Four Basis Conformations of Cycloheptane^a

param	B	TB	C	TC
sym	C ₂	C ₂	C _s	C ₂
variables	29	28	29	28
q ₂	1.163	1.163	0	0
φ ₂	0	90		
φ ₃	0	0	0.664	0.664
r(C1C2)	1.545	1.546	1.547	1.567
r(C2C3)	1.552	1.546	1.541	1.546
r(C3C4)	1.546	1.560	1.551	1.540
r(C4C5)	1.563	1.547	1.568	1.542
β(C7C1C2)	115.0	114.6	110.3	126.3
β(C1C2C3)	115.1	115.0	112.9	123.0
β(C2C3C4)	115.0	115.8	120.6	115.0
β(C3C4C5)	115.8	115.3	124.5	111.7
τ(C7C1C2C3)	-57.8	-45.5	-83.0	-20.6
τ(C1C2C3C4)	-30.9	66.0	69.1	55.1
τ(C2C3C4C5)	69.8	15.6	-40.0	-77.9
τ(C3C4C5C6)	0	-70.8	0	87.1
abs E (STO-3G)	-270.044 25	-270.044 23	-270.033 45	-270.032 75
rel E	0	0.01	6.78	7.22

^aPuckering amplitudes and bond lengths in Å, angles in deg, absolute energies in hartrees, relative energies in kcal/mol.

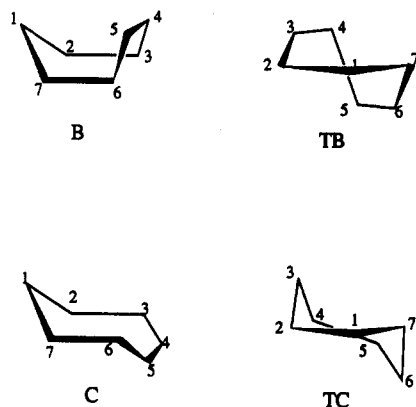


Figure 4. Basis conformations of cycloheptane.

to be optimized. Convergence was achieved in 19 (B), 14 (TB), 14 (C), and 11 (TC) optimization steps leading to time savings between 30 and 50% compared to geometry optimizations with the same starting geometry but using dihedral angles rather than puckering coordinates.

B and TB conformation form the first pseudorotational family of the seven-membered ring that is described by the puckering coordinates q_2 and ϕ_2 . Similarly, C and TC conformation constitute the second pseudorotational family that is described by q_3 and ϕ_3 .

The calculated puckering amplitudes reveal that B and TB form on the one side and C and TC form on the other side are equally puckered. Puckering of C and TC, however, is just 60% of that of B and TB. The calculated energies (Table II) reflect the similarity of the puckering amplitudes for B and TB as well as for C and TC. The energies suggest that within the B-TB family pseudorotation is free, while in the C-TC family there is a small barrier to pseudorotation (Table II).

Since the C form is less puckered than the B form, eclipsing of CH bonds is less effectively avoided and, accordingly, the relative energy of C is 6.8 kcal/mol higher than that of B. A similar observation can be made for the TC that is 7.2 kcal/mol higher in energy than the TB. However, the C and the TC form can be stabilized by appropriate admixtures of B and TB form (Table III). For example, the C becomes more stable by 9.5 kcal/mol due to an admixture of 32% of an inverted B ($\phi_3 = 180^\circ$). In this way, the top part of the chair (atoms 6, 7, 1, 2, 3) becomes flatter while the lower part (atoms 2, 3, 4, 5, 6, 7) becomes steeper. The result is an improved staggering of the methylene groups in the lower part and a stabilization of the C. Stabilization is partially offset by increased eclipsing of CH₂ groups

TABLE III: Energies and Optimized Geometries of Cycloheptane Conformations after Mixing of Basis Conformations^a

param	B	TB	C	TC
sym	C ₂	C ₂	C _s	C ₂
variables	30	29	30	29
q ₂	1.162	1.161	0.456	0.526
% B or TB ^b	100	100	31.6	38.7
φ ₂	0	90	180	90
q ₃	0.010	0.010	0.670	0.662
% C or TC ^b	0	0	68.4	61.3
φ ₃	180	270	0	90
Q ^c	1.162	1.161	0.810	0.846
r(C1C2)	1.545	1.546	1.443	1.549
r(C2C3)	1.552	1.546	1.547	1.548
r(C3C4)	1.547	1.559	1.546	1.547
r(C4C5)	1.563	1.546	1.560	1.545
β(C7C1C2)	115.6	115.0	114.9	116.3
β(C1C2C3)	115.2	115.3	114.4	115.6
β(C2C3C4)	114.7	115.8	114.7	113.2
β(C3C4C5)	115.7	115.0	117.7	115.4
τ(C7C1C2C3)	-56.5	-45.1	-63.3	-38.6
τ(C1C2C3C4)	-31.9	64.6	83.9	86.7
τ(C2C3C4C5)	70.3	17.1	-66.5	-71.8
τ(C3C4C5C6)	0	-72.6	0	54.6
abs E (STO-3G)	-270.044 29	-270.044 27	-270.040 43	-270.050 11
rel E	3.65	3.66	0.99	0
abs E (6-31G*)	-273.223 41	-273.223 40	-273.228 06	-273.229 56
rel E	3.86	3.86	0.94	0

^aPuckering amplitudes and bond lengths in Å, angles in deg, absolute energies in hartrees, relative energies in kcal/mol. The ring forms are named according to the basis conformation that dominates the character of the ring. ^bGiven by $100(q_2^2/Q^2)$ and $100(q_3^2/Q^2)$, respectively. ^c $Q = (q_2^2 + q_3^2)^{1/2}$ denotes the total puckering amplitude.²

in the upper part of the C, but since the first effect dominates an overall increase in the stability of the C from mixing in the B results (Table III).

In a similar way, the stability of the TC form is increased by an admixture of the twist-boat form. This causes improved staggering at bonds C1C2, C2C3, C4C5, C6C7, and C7C1 as can easily be verified by inspection of Figure 4. Comparison of the optimized puckering amplitudes reveals that 39% of the TB form and 61% of the TC form lead to the most stable conformation of cycloheptane, which is 1 kcal/mol more stable than the C form with the 32% admixture of the B form. Hence, pseudorotation between these conformations will be hindered by a barrier of at least 1 kcal/mol.

B and TB form mix only negligibly with C and TC form (Table III). Their energies are almost identical, namely, 3.7 kcal/mol above that of the TC form. This order of stabilities is confirmed by HF/6-31G*//HF/STO-3G calculations (Table III). Furthermore, our results are in line with force-field investigations of cycloheptane published by various authors.^{31,32} For example, calculated relative energies obtained by Allinger are in good agreement with the values obtained in this work. The experimental evidence available so far points also to the TC form as the most stable cycloheptane conformation.³¹

Conclusion

Analytical gradients can be easily extended for the use of puckering coordinates in geometry optimizations of ring molecules. The necessary formulas have been given and tested for eight conformations of cycloheptane. Results show that the use of the puckering coordinates leads to time savings between 20 and 50% in geometry optimizations of puckered *N*-membered rings. It has to be stressed that the puckering coordinates become particularly useful for geometry optimization and conformational analysis of larger puckered *N*-membered rings.³³

(31) See, e.g.: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177, American Chemical Society: Washington, D.C., 1982; p 98, and references therein.

(32) It is interesting to note that Bocian et al. (Bocian, D. F.; Pickett, H. M.; Rounds, T. C.; Strauss, H. L. *J. Am. Chem. Soc.* 1975, 97, 687) derived for the seven-membered ring a set of internal coordinates that is similar to the puckering coordinates.

Appendix: The Invariance of the Mean Plane

The mean plane will be an appropriate reference plane if it does not change during a conformational process such as ring pseudorotation or ring inversion. In the past, criticism has been raised that in the original derivation of the mean plane² no proof on the invariance of the mean plane has been given. It has been claimed that the normal of the mean plane is not invariant but precesses under pseudorotation.²⁵ Therefore, we prove now that the mean plane is indeed invariant and that previous criticism with regard to this point is unjustified.

For a given conformer C_1 of a puckered N -membered ring its $N-3$ puckering parameters $\{q_m, \phi_m\}$ and, hence, the orientation of the mean plane are considered to be known. Accordingly, the z_j coordinates of C_1 fulfil eqs 4–6.

Any conformational change of the N -membered ring will lead to a new conformer C_2 and a new set of puckering coordinates $\{q_m', \phi_m'\}$. The coordinates z_j' of C_2 are given by eqs A1 and A2:

$$z_j' = (2/N)^{1/2} \sum_{m=2}^{(N-1)/2} q_m' \cos(\phi_m' + m\alpha_j) \quad (\text{A1})$$

$z_j' =$

$$(2/N)^{1/2} \sum_{m=2}^{(N-1)/2} q_m' \cos(\phi_m' + m\alpha_j) + (1/N)^{1/2} q_{N/2} (-1)^{j-1} \quad (\text{A2})$$

The coordinates x_j' and y_j' of C_2 are found in the way described in section 5.

To prove that the mean plane of any puckered N -membered ring is invariant with regard to any conformational change, it suffices to show that the mean plane of conformer C_1 is identical with that of conformer C_2 . The identity of the two mean planes follows immediately if the z_j' coordinates of eqs A1 and A2 fulfil equations 4–6. For reasons of simplicity, we will show this first for an odd-membered ring and, then, for an even-membered ring.

Insertion of eqs A1 and A2 into (4)–(6) leads to eqs A3–A5, where the exclamation mark indicates that the vanishing of the sums has yet to be proven:

$$(2/N)^{1/2} \sum_{j=1}^N \sum_{m=2}^{(N-1)/2} q_m' \cos(\phi_m' + m\alpha_j) \stackrel{!}{=} 0 \quad (\text{A3})$$

$$(2/N)^{1/2} \sum_{j=1}^N \sum_{m=2}^{(N-1)/2} q_m' \cos(\phi_m' + m\alpha_j) \cos \alpha_j \stackrel{!}{=} 0 \quad (\text{A4})$$

$$(2/N)^{1/2} \sum_{j=1}^N \sum_{m=2}^{(N-1)/2} q_m' \cos(\phi_m' + m\alpha_j) \sin \alpha_j \stackrel{!}{=} 0 \quad (\text{A5})$$

Equations A3–A5 can be rearranged to (A6)–(A8):

$$(2/N)^{1/2} \sum_{j=1}^N \sum_{m=2}^{(N-1)/2} q_m' \cos \phi_m' \cos(m\alpha_j) - q_m' \sin \phi_m' \sin(m\alpha_j) \stackrel{!}{=} 0 \quad (\text{A6})$$

$$(2/N)^{1/2} \sum_{j=1}^N \sum_{m=2}^{(N-1)/2} q_m' \cos \phi_m' \cos(m\alpha_j) \cos \alpha_j - q_m' \sin \phi_m' \sin(m\alpha_j) \cos \alpha_j \stackrel{!}{=} 0 \quad (\text{A7})$$

$$(2/N)^{1/2} \sum_{j=1}^N \sum_{m=2}^{(N-1)/2} q_m' \cos \phi_m' \cos(m\alpha_j) \sin \alpha_j - q_m' \sin \phi_m' \sin(m\alpha_j) \sin \alpha_j \stackrel{!}{=} 0 \quad (\text{A8})$$

At this point, it is convenient to transform from $N-3$ linearly independent hypercylindrical coordinates $\{q_m', \phi_m'\}$ to $N-3$ linearly independent rectangular coordinates $\{\xi_m', \eta_m'\}$:

$$q_m' \cos \phi_m' = \xi_m' \quad (\text{A9})$$

$$q_m' \sin \phi_m' = \eta_m' \quad (\text{A10})$$

With the rectangular coordinates ξ_m' and η_m' eqs A6–A8 change to (A11)–(A13):

$$(2/N)^{1/2} \sum_{m=2}^{(N-1)/2} [\xi_m' \sum_{j=1}^N \cos(m\alpha_j) - \eta_m' \sum_{j=1}^N \sin(m\alpha_j)] \stackrel{!}{=} 0 \quad (\text{A11})$$

$$(2/N)^{1/2} \sum_{m=2}^{(N-1)/2} [\xi_m' \sum_{j=1}^N \cos(m\alpha_j) \cos \alpha_j - \eta_m' \sum_{j=1}^N \sin(m\alpha_j) \cos \alpha_j] \stackrel{!}{=} 0 \quad (\text{A12})$$

$$(2/N)^{1/2} \sum_{m=2}^{(N-1)/2} [\xi_m' \sum_{j=1}^N \cos(m\alpha_j) \sin \alpha_j - \eta_m' \sum_{j=1}^N \sin(m\alpha_j) \sin \alpha_j] \stackrel{!}{=} 0 \quad (\text{A13})$$

These equations can be solved by applying the trigonometric relationships A14–A19:

$$\sum_{j=1}^N \cos(m\alpha_j) = 0 \quad (\text{A14})$$

$$\sum_{j=1}^N \sin(m\alpha_j) = 0 \quad (\text{A15})$$

$$\sum_{j=1}^N \cos(m\alpha_j) \cos \alpha_j = 0 \quad (\text{A16})$$

$$\sum_{j=1}^N \cos(m\alpha_j) \sin \alpha_j = 0 \quad (\text{A17})$$

$$\sum_{j=1}^N \sin(m\alpha_j) \cos \alpha_j = 0 \quad (\text{A18})$$

$$\sum_{j=1}^N \sin(m\alpha_j) \sin \alpha_j = 0 \quad (\text{A19})$$

with $\alpha_j = 2\pi(j-1)/N$. Thus, for each $m = 2, \dots, (N-1)/2$, eqs A11–A13 are correct. In view of (A9) and (A10) the same holds for eqs A3–A5. From (A1) it follows that

$$\sum_j z_j' = 0 \quad (\text{A20})$$

$$\sum_j z_j' \cos \alpha_j = 0 \quad (\text{A21})$$

$$\sum_j z_j' \sin \alpha_j = 0 \quad (\text{A22})$$

which means that the new conformer C_2 possesses the same mean plane as conformer C_1 . Since no restrictions have been made when going from C_1 to C_2 , eqs A20–A22 are correct for all conformers in the conformational space of an odd-membered ring of size N . In other words, conformational processes such as pseudorotation or inversion do not change the orientation of the mean plane.

If N is even, a set of equations similar to (A3)–(A5) can be derived. These new equations contain an extra term resulting from $q_{N/2}'$ in eq A2. There are now $(N-4)$ transformation equations (A9) and (A10) and an additional equation that associates the rectangular coordinate ν' to the puckering amplitude $q_{N/2}'$:

$$q_{N/2}' = \nu'$$

Equations A11–A13 have to be extended by the ν' contributions, which vanish because of (A14) and (A15). Again, eqs A20–A22 are fulfilled. This proves that the mean plane is invariant for all conformational processes involving either odd- or even-membered rings of size N .

It has been shown that the LSP is not identical with the mean plane and that it takes a new orientation for each conformer considered.¹¹ In a conformational process the normal of the LSP

(33) Cremer, D., to be published.

(34) See, e.g.: Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* 1979, 101, 2550.

precesses around the normal of the mean plane. Hence, the LSP is not a suitable reference plane for investigation puckered rings.

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Registry No. Cycloheptane, 291-64-5.

Nonadditivity of Interaction in Hydrated Cu^+ and Cu^{2+} Clusters

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Two- and three-body interaction energies are calculated by using ab initio molecular orbital theory for tetrahedral, octahedral, and cubic arrangements of H_2O molecules around Cu^+ and Cu^{2+} ions in $[\text{Cu}(\text{OH}_2)_n]^{q+}$ clusters to assess the nonadditivity of interactions in hydrated transition-metal-ion clusters. The results are compared to full many-body results for the clusters. For Cu^{2+} there appears to be a slow convergence of the interaction terms to the full many-body result. For Cu^+ many-body effects are much less important, although a surprising result is the finding that the second water molecule is bound more strongly to Cu^+ than the first water molecule in a $[\text{Cu}(\text{OH}_2)_2]^+$ cluster when the O-Cu-O angle is 180° . More detailed investigation of $[\text{Cu}(\text{OH}_2)]^+$ and $[\text{Cu}(\text{OH}_2)_2]^+$ clusters confirmed this result and also revealed that the $n = 2$ cluster is characterized by a shorter CuO distance than the $n = 1$ cluster. Neither the increase in binding nor contraction of the CuO distance occurs in $[\text{Cu}(\text{OH}_2)_n]^{2+}$ clusters in going from $n = 1$ to $n = 2$ or in clusters containing non-transition-metal monocations such as Li^+ or Na^+ .

I. Introduction

The simulations of multivalent transition-metal ions in water play an important role in development of theoretical models of electron transfer in aqueous systems¹ as well as other areas of solution chemistry. Ion-water pair potentials derived from ab initio molecular orbital theory have been used in molecular dynamics and Monte Carlo simulations of metal cations in water²⁻¹¹ with varying degrees of success, because of problems with nonadditivity. Nonadditivity has been studied for a number of ion-water interactions.¹²⁻¹⁶ Most of this work has concentrated on non-transition-metal ions including Li^+ ,^{12,13} Na^+ ,¹⁶ Be^{2+} ,^{11,14} Mg^{2+} ,^{15,16} Ca^{2+} ,¹⁵ and Al^{3+} .¹⁶ As part of a molecular dynamics study of Fe^{2+} and Fe^{3+} in water, we recently reported⁸ on the nonadditivity of ab initio ion-water pair potentials for these two transition-metal ions which indicated that three-body interaction terms were very substantial. A subsequent more extensive study¹⁷ of Fe^{3+} in water indicated a slow convergence of the two-, three-, and four-body interaction energies to the to the full many-body result.

In this paper we report on a study using ab initio molecular orbital theory to assess nonadditivity in interactions of Cu^+ and Cu^{2+} with water. We have carried out a systematic calculation of the two- and three-body interaction terms for $[\text{Cu}(\text{OH}_2)_n]^{2+}$ and $[\text{Cu}(\text{OH}_2)_n]^+$ clusters with $n = 4, 6, 8$ for comparison to total interaction energies of the clusters. A surprising result of this study was that the three-body water-ion-water term is attractive (negative) for the Cu^+ ion with O-Cu-O angles of 180° . This result was investigated further by studying the $[\text{Cu}(\text{OH}_2)_2]^+$ and $[\text{Cu}(\text{OH}_2)]^+$ clusters at higher levels of calculation. It was found that the binding of the second water molecule to the cluster, $[\text{Cu}(\text{OH}_2)]^+ + \text{H}_2\text{O} \rightarrow [\text{Cu}(\text{OH}_2)_2]^+$, is larger than that of the first water molecule, $\text{Cu}^+ + \text{H}_2\text{O} \rightarrow [\text{Cu}(\text{OH}_2)]^+$. This unusual feature has recently been reported in some experimental studies of hydration energies of transition-metal monocations including Cu^+ .^{18,19} In section II, the theoretical methods and clusters studied are described. In section III, the results for the clusters are presented and discussed. In section IV higher level calculations are presented for $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_n]^+$ clusters with

$n = 1, 2$, and results for the binding of the second water molecule in the Cu^{2+} and Cu^+ clusters are compared.

II. Theoretical Methods

Energies for an m -body system may be expanded in a series of one, two, three, ..., m -body terms, as follows

$$E(X_1 X_2 \dots X_m) = \sum_{i=1}^m E^{(1)}(X_i) + \sum_{i>j=1}^m E^{(2)}(X_i X_j) + \sum_{i>j>k=1}^m E^{(3)}(X_i X_j X_k) + \sum_{i>j>k>l=1}^m E^{(4)}(X_i X_j X_k X_l) + \dots + \sum_{i>j>k\dots}^m E^{(m)}(X_i X_j X_k X_l \dots X_m) \quad (1)$$

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