Efficient Geometry Optimization of Molecular Clusters

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ABSTRACT: By combining valence coordinates (stretches, bends, and torsions) to describe *intramolecular* degrees of freedom with inverse distance coordinates for *intermolecular* degrees of freedom, we derive an efficient set of coordinates for the geometry optimization of molecular clusters. We illustrate the efficacy of our new coordinates by considering randomly generated clusters of dihydrogen and water molecules. Compared to optimizations in Cartesian coordinates, the number of cycles required for convergence is reduced by up to a factor of 30. In addition, for the dihydrogen clusters, optimizations using our new cluster coordinates consistently converge to lower energy structures than the corresponding Cartesian optimizations. Our method is far more efficient than optimizations using **Z**-matrix coordinates, and it avoids all problems with near-linear bond angles that are endemic with a **Z**-matrix description of the cluster geometry. Additionally, by constraining all the intramolecular degrees of freedom in a completely automated manner, we are able to carry out full rigid-body optimizations. © 2000 John Wiley & Sons, Inc.   J Comput Chem 21: 69–76, 2000

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Introduction

The efficient optimization of the geometries of weakly bound molecular clusters has long been a difficult task. Perhaps the major problem is that such systems comprise essentially two very different types of forces: strong intramolecular forces (chemical bonds) within the individual molecules,

and very much weaker intermolecular forces (e.g., van der Waals interactions, hydrogen bonds) acting between the molecules in the cluster. Typical coordinate systems (e.g., Cartesian coordinates, **Z**-matrix coordinates, or natural or delocalized internal coordinates) treat all intra- and intermolecular degrees of freedom in the same way. It would surely be more appropriate to choose coordinates that were in some way "tuned" for the different types of forces in the system being optimized.

Recently we proposed the use of inverse-power distance coordinates for the optimization of atomic

microclusters.[1] Test optimizations of clusters of up to 48 argon atoms using a simple 6–12 Lennard–Jones potential[2] clearly demonstrated that inverse-power distance coordinates were more efficient in terms of the number of cycles to reach convergence than either Cartesians, natural internal coordinates,[3] or delocalized internal coordinates[4] for these systems. We might expect such coordinates to be useful for describing the intermolecular interactions present in molecular clusters as well. Note that Simons et al. previously utilized a variable for the description of stretching potential curves that is equivalent to an inverse-distance coordinate.[5]

Given that suitable linear combinations of standard internal coordinates (stretches, bends, and torsions) are generally an excellent choice for optimizing molecular geometries, an obvious idea for molecular clusters is to mix the two types of coordinates, i.e., use stretches, bends, and torsions to describe the *intramolecular* degrees of freedom (the geometry of each individual molecule in the cluster) and inverse-power distance coordinates for the weaker *intermolecular* degrees of freedom. Mixed coordinates have been used in the past, but these have been confined almost entirely to mixed Cartesian/valence coordinates. For example, Nakano et al.[6] and later Schlegel[7] used Cartesian coordinates to describe the cyclic part of a molecule, with Z-matrix coordinates to describe the remaining (acyclic) part, and Head[8] used mixed Cartesian/internal coordinates to model chemisorption with the (fixed) model surface described using Cartesians and internal coordinates used for the adsorbate.

In this article we demonstrate the utility of our mixed internal/inverse-power distance coordinates for the optimization of molecular clusters. First we briefly summarize the theoretical background to the general internal coordinate scheme used in this work. Then we carry out optimizations on randomly generated clusters of 10 dihydrogen and 10 water molecules and compare the performance of our new cluster coordinates with Cartesian, simple distance, and Z-matrix coordinates. Finally, we show how, by constraining all the intramolecular degrees of freedom, it is possible to carry out full rigid-body optimizations.

Theoretical Background

The background to optimization in redundant internal coordinates is now well established, and stems from the 1992 article of Pulay and Fogarasi[9]

and the later work of Baker et al.[4] The geometry of the system is described using a set of n, in general redundant, internal coordinates, $\mathbf{q} = \{q_1, q_2, \ldots, q_n\}^T$. Small displacements $\Delta\mathbf{q}$ in $\mathbf{q}$ are related to the corresponding Cartesian displacements, $\Delta\mathbf{x}$, by means of the well-known $\mathbf{B}$ matrix[10]:

$$\Delta\mathbf{q} = \mathbf{B}^q\Delta\mathbf{x}. \tag{1}$$

Diagonalization of the $n \times n$ symmetric matrix $\mathbf{G} = \mathbf{B}^q(\mathbf{B}^q)^T$ results in two sets of eigenvectors: a set of $m = 3N - 6$ (where N is the number of atoms) *nonredundant* eigenvectors with eigenvalues $\lambda > 0$, and a set of $n - m$ *redundant* eigenvectors with eigenvalues $\lambda = 0$. The eigenvalue equation for $\mathbf{G}$ can be written as

$$\mathbf{G}(\mathbf{U} \quad \mathbf{R}) = (\mathbf{U} \quad \mathbf{R})\begin{pmatrix} \mathbf{\Lambda} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \tag{2}$$

where $\mathbf{U}$ is the set of nonredundant eigenvectors of $\mathbf{G}$ and $\mathbf{R}$ is the redundant set. In this way there is a natural separation of the redundant and nonredundant subspaces of our original coordinate space; the former can be discarded.

In this work, the primitive coordinate set $\mathbf{q}$ consists of all stretches, all planar bends, and all proper torsions that can be generated based on the atomic connectivity (bonding) *within* each individual molecule in the cluster, together with all possible (inverse) distances between atoms belonging to *different* molecules in the cluster. For example, for a cluster of 10 water molecules, $\mathbf{q}$ would comprise two O—H stretches and one ∠HOH bend for each water molecule in the cluster (30 primitives), plus potentially 405 inverse distances between the atoms in different water molecules. In practice a cutoff can be used to reduce the number of inverse-distance coordinates; for example, only inverse distances between atoms that are less than a certain distance apart (say 5–7 Å) are actually taken.

All these coordinates are used to form and diagonalize the $\mathbf{G}$ matrix [eq. (2)]. In our current algorithm[11] we do not do a full diagonalization of $\mathbf{G}$; instead only the highest $3N - 6$ (where N is the total number of *atoms* in the cluster) eigenvalues are determined,[12] with the corresponding eigenvectors defining the transformation matrix $\mathbf{U}$. Note that each eigenvector of $\mathbf{G}$ is a linear combination of all the initial primitives (stretches, bends, and inverse distances); the $3N - 6$ vectors in $\mathbf{U}$ define a transformation of the original redundant set of primitives, $\mathbf{q}$, into a complete set of nonredundant coordinates.

Once the initial transformation matrix $\mathbf{U}$ defining the set of nonredundant coordinates has been obtained, there are essentially three possibilities on

subsequent optimization cycles: (i) retain the same set of coordinates (i.e., the same $\mathbf{U}$) throughout the optimization; (ii) using the *same* underlying set of primitives, $\mathbf{q}$, repeat the diagonalization [i.e., the solution of eq. (2)] at the start of each cycle, which typically gives a different transformation matrix, $\mathbf{U}$ (i.e., a different set of coordinates); or (iii) repeat the solution of eq. (2) with a *modified* set of primitives (i.e., use a different $\mathbf{U}$ *and* a different $\mathbf{q}$).

Standard practice for "normal" molecular optimizations is option (i). Experience with argon clusters[1] has shown that initial guess starting geometries are often markedly different from the final converged structures, and in the early stages of the optimization changes in geometry are significant. Consequently, coordinates generated at the beginning of the optimization are not always appropriate for its final stages, and for cluster optimizations, options (ii) and (iii) are more appropriate. If distance cutoffs are used the underlying primitive space can change between cycles and option (iii) is then mandatory.

Once our set of delocalized cluster coordinates has been defined, the gradient is iteratively transformed from Cartesian coordinates into internals by applying the conjugate gradient method[11, 13] to the equation

$$\mathbf{g}^{\text{int}}(k + 1) = \mathbf{D}^{-1}\big[\mathbf{Bg}^{\text{cart}} + \big(\mathbf{D} - \mathbf{BB}^{\text{T}}\big)\mathbf{g}^{\text{int}}(k)\big], \quad (3)$$

where $\mathbf{B} = \mathbf{U}^{\text{T}}\mathbf{B}^{\mathbf{q}}$ and $\mathbf{D}$ is the diagonal part of $\mathbf{BB}^{\text{T}}$. Note that the $\mathbf{BB}^{\text{T}}$ matrix is never explicitly constructed; the vector quantity $\mathbf{BB}^{\text{T}}\mathbf{g}^{\text{int}}(k)$ is formed by two matrix vector multiplications. On any optimization cycle in which eq. (2) is solved to (re)generate $\mathbf{U}$, then eq. (3) converges in one cycle because $\mathbf{BB}^{\text{T}} = \mathbf{D}$ and $\mathbf{g}^{\text{int}}$ is given by the first term on the right hand side of eq. (3).

Following transformation of the gradient, the new optimization step is formed using the current geometry, $\mathbf{g}^{\text{int}}$, and (optionally) the Hessian matrix, $\mathbf{H}^{\text{int}}$, or, more usually, an approximation to it. After the new geometry in internal coordinates is obtained, it has to be converted back into Cartesians to calculate a new energy and gradient for the next optimization step. This is the backtransformation step, which is also accomplished iteratively, according to

$$\mathbf{x}(k + 1) = \mathbf{x}(k) + \big(\mathbf{BB}^{\text{T}}\big)^{-1}\mathbf{B}(k)\big[\mathbf{s} - \mathbf{s}(k)\big]. \quad (4)$$

Here $\mathbf{s}$ is the (known) new geometry in internal coordinates and the iterative procedure is typically started ($k = 1$) using the *old* Cartesian geometry (and the old $\mathbf{B}$ matrix). The procedure is terminated when the internal coordinates $\mathbf{s}(k)$ generated on the kth iteration from the Cartesian set $\mathbf{x}(k)$ are identical to $\mathbf{s}$ within a given tolerance. For more details of all the transformations involved, see ref. 11.

Results

We tested our new cluster coordinates on randomly generated clusters of 10 hydrogen molecules and 10 water molecules, respectively. The dihydrogen clusters were generated in a similar manner to the argon clusters in ref. 1; for the water clusters we used a $\mathbf{Z}$ matrix with the oxygen atom of each water molecule "attached" to a hydrogen of the previously defined water molecule by a "bond" distance of between 2.5 and 4.0 Å, making an angle with the oxygen atom of the previous water of between 60° and 175° and a random dihedral angle with the other hydrogen. Using a $\mathbf{Z}$ matrix enables us to directly compare optimizations using our cluster coordinates with $\mathbf{Z}$-matrix optimizations.

All hydrogen molecules in our dihydrogen clusters were given an initial H—H bond length of 0.72 Å, and all water molecules in the water clusters had initial O—H bond lengths of 0.966618 Å and ∠HOH bond angles of 107.6823°; in the latter case these were the optimized parameters for the isolated molecule at the level of theory chosen for our study, RHF/3-21G. For the hydrogen clusters we used 10 H—H stretches and all possible intermolecular inverse H—H distances (180 in total) for our initial set of primitives; for the water clusters we carried out optimizations using all possible (405) intermolecular inverse distances and with various cutoffs.

As noted in the previous section, the transformation matrix $\mathbf{U}$ defining the set of nonredundant delocalized cluster coordinates was regenerated at the start of each optimization cycle. All optimizations were started with a default Hessian diagonal in the *primitive* space, and diagonal force constants of 0.5 au for regular stretches and 0.2 au for bends and inverse distances. On subsequent cycles this was updated using a standard BFGS update.[14] Details of how to carry out the Hessian update when the cluster coordinates (and possibly the underlying primitives themselves) are changing are given in ref. 1. The Cartesian optimizations were started with a unit Hessian matrix.

Table I gives the starting energies, the number of cycles to converge, and the final energies for 20 randomly generated clusters, each containing 10 hydrogen molecules: the optimizations were carried

TABLE I.

Starting Energy, Number of Cycles to Converge, and Final Energy for RHF/3-21G Optimizations of 20 Randomly Generated Clusters of 10 H_2 Molecules.

Cluster	Starting Energy	Cartesian		Distance		New Internal[a]	
		Cycles	Energy[b]	Cycles	Energy[b]	Cycles	Energy[b]
1	−11.166613	613	−11.230147	328	−11.230102	34	−11.230188
2	−11.151158	506	−11.230130	349	−11.230138	33	−11.230208
3	−11.159068	282	−11.230023	219	−11.230007	30	−11.230193
4	−11.142043	100	−11.229742	222	−11.230099	55	−11.230162
5	−11.177657	776	−11.230133	234	−11.230058	24	−11.230170
6	−11.178220	305	−11.229987	209	−11.230027	58	−11.230176
7	−11.150748	338	−11.230103	226	−11.230106	31	−11.230226
8	−11.152618	410	−11.230122	325	−11.230153	47	−11.230212
9	−11.170617	454	−11.230144	257	−11.230097	17	−11.230226
10	−11.148964	425	−11.230093	313	−11.230126	42	−11.230196
11	−11.157261	431	−11.230073	312	−11.230129	70	−11.230190
12	−11.171696	501	−11.230054	303	−11.230045	39	−11.230223
13	−11.161546	500	−11.230130	235	−11.230112	66	−11.230223
14	−11.164816	435	−11.230041	282	−11.230045	33	−11.230176
15	−11.143458	478	−11.230110	230	−11.230083	32	−11.230226
16	−11.151136	965	−11.230106	287	−11.230126	54	−11.230208
17	−11.157329	555	−11.230116	221	−11.230013	33	−11.230206
18	−11.171771	357	−11.230074	287	−11.230116	41	−11.230190
19	−11.141685	172	−11.229711	267	−11.230112	39	−11.230206
20	−11.150264	307	−11.230016	267	−11.230084	35	−11.230202
Average		446	−11.230053	269	−11.230089	41	−11.230200

The initial bond length was 0.72 Å.

[a] Intermolecular cluster coordinates were based on simple inverse distances ($1/R$).

[b] Convergence criteria were a maximum gradient component of <0.00005 au and an energy change of $<10^{-7}$ hartree.

out in Cartesian coordinates, distance coordinates, and in our new delocalized cluster coordinates. For the intermolecular cluster coordinates we used simple inverse distances ($1/R$). Distance coordinates were derived in essentially the same way as our cluster coordinates, only instead of taking inverse distances as the intermolecular coordinates we used normal distances. Convergence criteria were a maximum gradient component of magnitude less than 5×10^{-5} au and an energy change from the previous cycle of less than 10^{-7} hartree. The maximum allowed step size during the optimizations was 0.3 (within the given coordinate space).

As can be seen from Table I, the number of cycles required to reach convergence using the new delocalized cluster coordinates compared to Cartesians is reduced, on the average, by at least an order of magnitude and in some cases by greater than 30. Furthermore, the final converged energy is *lower* in every single case with our cluster coordinates than with Cartesians. Because the intermolecular forces are so weak in this system, the Cartesian optimiza-

tions converge extremely slowly with (toward the end of the optimization) very small energy changes (10^{-6} hartree and less) between cycles. Such small energy changes cause the Cartesian optimizations to in effect converge prematurely, and this is one of the reasons why the final energies are all noticeably higher with Cartesian coordinates than for the corresponding optimization using delocatized cluster coordinates. This aspect of Cartesian optimizations has been commented upon previously.[4] Thus, the reduction in the number of cycles with cluster coordinates would be even greater if one considered convergence to the *same* energy.

Distance coordinates perform, on the average, better than Cartesians with a reduction in the number of cycles to converge by a factor of slightly less than 2. However, they are clearly nowhere near as efficient as cluster coordinates, showing the efficacy of using inverse distances for the intermolecular interactions as opposed to simple distances. Like Cartesians, distance coordinates tend to converge prematurely for weakly bound systems; they also

TABLE II.

Starting Energy, Number of Cycles to Converge, and Final Energy for RHF/3-21G Optimizations of 20 Randomly Generated Clusters of 10 Water Molecules.

		Cartesian		5/R No Cutoff		5/R 7 Å Cutoff		5/R 5 Å Cutoff	
Cluster	Starting Energy	Cycles	Energy	Cycles	Energy	Cycles	Energy	Cycles	Energy
1	−755.115211	534	−756.155574	106	−756.136180	88	−756.139218	72	−756.160624
2	−754.053552	570	−756.134288	104	−756.132959	77	−756.137779	76	−756.137143
3	−755.881811	803	−756.141558	114	−756.140620	149	−756.135688	95	−756.135594
4	−753.748264	574	−756.023863	117	−756.008779	79	−756.005086	79	−756.005086
5	−755.896953	1185	−756.138455	138	−756.154006	149	−756.154006	171	−756.145149
6	−755.898083	1062	−756.131668	74	−756.078492	157	−756.156160	96	−756.137849
7	−755.821867	824	−756.153424	73	−756.132446	80	−756.128552	80	−756.148429
8	−755.892869	949	−756.172644	148	−756.151254	Failed, bad Hessian update		96	−756.146477
9	−755.909313	560	−756.085270	57	−756.078492	59	−756.078492	99	−756.143112
10	−754.886028	432	−756.166936	93	−756.156803	87	−756.137979	67	−756.145506
11	−755.380782	492	−756.163356	93	−756.159235	74	−756.148729	62	−756.152696
12	−755.079338	531	−756.163372	71	−756.145844	73	−756.146042	73	−756.146042
13	−755.827660	716	−756.139681	118	−756.158240	89	−756.129679	82	−756.124723
14	−754.789518	935	−755.998054	172	−756.008601	130	−756.013627	Failed, bad Hessian update	
15	−754.751183	465	−756.163161	123	−756.160074	78	−756.164546	79	−756.160074
16	−755.735244	703	−756.152903	97	−756.138366	145	−756.163821	81	−756.136690
17	−755.811031	361	−756.152287	64	−756.152287	65	−756.152287	65	−756.152287
18	−755.863344	392	−756.119484	139	−756.149210	179	−756.149210	173	−756.144712
19	−755.758661	406	−756.142263	98	−756.161874	65	−756.158696	53	−756.158513
20	−755.738806	SCF convergence problems		84	−756.166069	98	−756.156687	59	−756.136633
Average		658	−756.131486	104	−756.128492	101	−756.129278	87	−756.137755

The initial O—H bond length was 0.966618 Å, and the initial ∠HOH bond angle was 107.6823.

tend to develop very small ($<10^{-4}$ au) Hessian eigenvalues (for the longer distance coordinates), which again hinder convergence.

Results for the water clusters are shown in Table II. The intermolecular cluster coordinates adopted for the water clusters were somewhat different than those taken for hydrogen; we used scaled inverse distances (specifically $5/R$) instead of simple inverse distances ($1/R$). Scaling was needed because using simple $1/R$ coordinates often resulted in considerable energy oscillation and convergence problems in the backtransformation. This was due to steps in the internal coordinate space being very large when transformed back into Cartesians; scaling the inverse distances reduced the step size in Cartesian space. The forces (hydrogen bonds) between water molecules in the water clusters are much stronger than the very weak van der Waals interactions between hydrogen molecules in the dihydrogen clusters, and similar changes in geometry result in much greater energy changes in the water than in the hydrogen clusters.

In addition to Cartesian optimizations, three sets of delocalized cluster coordinate results are reported in Table II; these have no cutoff for the intermolecular inverse distances (i.e., all 405 inverse distances are included in the primitive space), and cutoffs of 7 and 5 Å, respectively (i.e., only intermolecular distances of these values or less were included in the primitive space). We do not report the results of **Z**-matrix optimizations in Table II; in every case we tried, optimizations using these coordinates failed due to primitive bond angles exceeding 180° at some stage during the optimization. This is not surprising given that the optimum H—O···H hydrogen bond between two water molecules is near linear.

As can be seen, all three sets of internal cluster coordinate optimizations show a reduction in the number of cycles to converge compared to Cartesians, although this is not as great with the water clusters as it was for hydrogen. (At least part of the reason for this was the scaling of the inverse-distance coordinates.) However, it is still significant, on average by a factor of between 6 and 7, depend-

TABLE III.

Starting Energy, Number of Cycles to Converge, and Final Energy for RHF/3-21G Optimizations of Random Molecular Clusters.

Cluster	Starting Energy	Cartesian		Cluster[a]	
		Cycles	Energy[b]	Cycles	Energy[b]
$(CH_3)_2CO + C_2H_5OH + C_2H_4$	−421.558559	430	−421.735388	42	−421.731469
$(CH_3)_2O + H_2O + CH_3OH$	−343.189321	380	−343.224076	64	−343.244245
$4 \times CH_4$	−159.851475	26	−159.907963	42	−159.908309
$C_2H_6 + C_2H_4 + H_2O_2 + CH_4$	−346.309922	274	−346.322485	84	−346.323149
$6 \times C_2H_4$	−465.586061	417	−465.614752	152	−465.616508

[a] Intermolecular cluster coordinates were based on scaled inverse distances $(5/R)$ with a 5- or 7-Å cutoff.
[b] Convergence criteria were a maximum gradient component of <0.00005 au and an energy change of $<10^{-7}$ hartree.

ing on which coordinates are compared. Unlike the hydrogen clusters, water cluster optimizations using the new cluster coordinates do not always converge to lower energy structures than the corresponding Cartesian optimizations—about half the time the final converged energy is lowest for the Cartesian optimization. To give a rough measure of overall performance, we adopted the same technique that we used during our earlier work on argon clusters[1]: comparing the *average* final energy and *average* number of cycles to converge over all 20 cluster optimizations. Note that, due to convergence problems in the self-consistent field or to a bad Hessian update,* three of the coordinate sets failed to converge for one (a different one in each case) of the clusters; consequently, the average reported here is over 19 clusters. These values are given at the bottom of Table II (see also Table I) and suggest that *overall* the best choice of coordinates (of those tried) are $5/R$ cluster coordinates with a 5 Å cutoff; these converge on average nearly 8 times faster than Cartesians and to a lower average energy, although on a case by case basis each coordinate choice converges to the lowest energy roughly equally.

Table III presents results for a number of smaller clusters containing different (and somewhat larger) molecules. For the intramolecular coordinates the dihydrogen clusters have only a single bond length, the water clusters have just two bond lengths and one angle, and there are no redundancies; the results presented in Table III show that our new cluster coordinates are just as applicable to clusters of larger molecules with redundancies in the intramolecular coordinate space. Note that with the exception of the

methane and ethylene clusters (entries 3 and 5 in Table III) the geometries of the individual molecules in the clusters were only approximate and were not optimal for the level of theory used (RHF/3-21G).

For all the clusters shown in Table III except one, optimizations using cluster coordinates converged to a *lower* energy structure than the corresponding Cartesian optimization and, again with one exception, took far fewer cycles. The energy exception was the $(CH_3)_2CO + C_2H_5OH + C_2H_4$ cluster, which converged to a lower energy but took over an order of magnitude more cycles. The Cartesian optimization on the four molecule methane cluster converged in fewer cycles, but even here the energy was lower after just six cycles of the cluster coordinate optimization than at the final converged Cartesian geometry.

Rigid-Body Optimization

Rigid-body optimization is a complex problem in geometry optimization. When the geometry of a collection or cluster of molecules, each of which is considered as a rigid body, is optimized, then the normal intramolecular degrees of freedom are frozen; and it is the translations and rotations of the molecules relative to each other, which are not considered at all in the optimization of *single* molecules, that are now the important degrees of freedom.

In his 1990 article,[15] King considered the optimization of rigid bodies in Cartesian coordinates. Each (rigid) molecule is assigned its own right-handed Cartesian coordinate frame attached to and rotating with the molecule. The origin of the molecular frame can be taken to be the center of mass. The molecular frame can be related to a (fixed) laboratory frame by three translational, **T**, and three

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*These calculations could be continued if desired by simply retracting the last step and either reinitializing the Hessian or skipping the update.

rotational, $\boldsymbol{\Phi}$, coordinates with the latter taken to be the three Cartesian components ϕ_x, ϕ_y, ϕ_z of the rotation vector. The transformation of gradients calculated in the laboratory frame to the molecular frame is discussed,[15] but no examples of real optimizations are given, the article being mainly pedagogical.

A more practical method of carrying out rigid-body optimizations is with a $\mathbf{Z}$ matrix. It is fairly straightforward to write a $\mathbf{Z}$ matrix for each molecule and connect one molecule to another by a distance (between two selected atoms, one from each molecule) and five bends, or a distance, two bends, and three torsions. The main problem with this approach is that the coordinates used to describe the intermolecular degrees of freedom are almost completely arbitrary and are likely to be very inefficient. Because in many cases it is not at all obvious what the final optimized cluster geometry will be, starting geometries are likely to be poor, particularly for larger clusters, and arbitrarily chosen bond angles will have a relatively high probability of tending toward 0° or 180° during the course of the optimization, causing the job to crash. Additionally, constructing the initial $\mathbf{Z}$ matrix can often be tedious, although, at least in principle, this can be automated.

By using the Schmidt orthogonalization scheme for imposing constraints introduced in the original delocalized internal coordinate article[4] we can effectively constrain all the intramolecular degrees of freedom in a molecular cluster and in this way carry out complete rigid-body optimizations. The relationship between weakly bound molecular clusters and rigid-body clusters is such that if cluster coordinates are eminently suitable for the former, as we have just demonstrated, they should be just as useful for the latter as well.

Full details of the Schmidt orthogonalization scheme are given in ref. 4. By projecting unit vectors (with unit components corresponding to those primitives you wish to constrain, in this case all the intramolecular degrees of freedom) onto the nonredundant subspace $\mathbf{U}$ of eq. (2) and Schmidt orthogonalizing the resultant vectors against all other vectors in $\mathbf{U}$, it is possible to isolate individual primitives in a consistent manner into *single* vectors. By removing these vectors from the active space, optimizations can be carried out in which the primitives involved retain their initial values throughout the optimization. Using this approach we can optimize just the intermolecular degrees of freedom and thus carry out full rigid-body optimizations.

We repeated the unconstrained dihydrogen cluster optimizations (Table I) treating the hydrogen molecules as rigid bodies and constraining all the H—H intramolecular distances at 0.72 Å. The results are shown in Table IV. As can be seen, rigid-body optimizations using inverse-distance coordinates are just as efficient (in terms of the number of cycles to reach convergence) as the corresponding unconstrained optimization. This is entirely as expected and confirms that inverse-distance coordinates are indeed an excellent choice for optimizing the geometries of molecular clusters, both unconstrained and rigid body. Nearly all of the rigid-body dihydrogen clusters converged to similar final geometries (except for the intramolecular H—H distances) as in the corresponding unconstrained optimization. Treating the hydrogen molecules as rigid bodies results in final energies that are around 0.00171 hartree (just over 1 kcal/mol) higher than in the fully relaxed case. Over all 10 molecules in the cluster, this is only 0.000171 hartree (0.1 kcal/mol) per H_2 molecule. Not surprisingly, this energy difference is almost entirely due to relaxation of the H—H bond distance in the unconstrained clusters (optimized RHF/3-21G H—H distance in H_2 is 0.7348 Å; energy difference between the minimum and an H—H distance of 0.72 Å is 0.000168 hartree).

We carried out full rigid-body optimizations with no difficulties on the five clusters shown in Table III. For example, the cluster of six ethylene molecules, taken as six rigid bodies, converges in 131 cycles to an energy of $-465.616447\ E_h$, which is only slightly higher than the fully relaxed system. The energy of six isolated ethylene molecules is $-465.605928\ E_h$. We should perhaps emphasize that starting geometries in all these clusters were essentially random, and a marked reduction in the number of optimization cycles is expected if more "sensible" initial geometries are used.

Summary

We have demonstrated that a new set of *delocalized cluster coordinates* in which *intramolecular* bonding is represented by standard stretches, bends, and torsions and *intermolecular* bonding by (scaled) inverse distances are far more efficient at optimizing the geometries of weakly bound molecular clusters than Cartesian coordinates, which are nearly always used for this purpose. In addition, because of the marked tendency for bond angles to change through 180° during cluster optimizations, our cluster coordinates, which have no angles involved in

TABLE IV.

Starting Energy, Number of Cycles to Converge, and Final Energy for RHF/3-21G Optimizations of 20 Randomly Generated Clusters of 10 H_2 Molecules.

| Cluster | Starting Energy | Unconstrained[a] | | Rigid Body H_2 | |
		Cycles	Energy[b]	Cycles	Energy[b]
1	−11.166613	34	−11.230188	35	−11.228479
2	−11.151158	33	−11.230208	34	−11.228498
3	−11.159068	30	−11.230193	30	−11.228483
4	−11.142043	55	−11.230162	44	−11.228449
5	−11.177657	24	−11.230170	24	−11.228462
6	−11.178220	58	−11.230176	59	−11.228468
7	−11.150748	31	−11.230226	33	−11.228515
8	−11.152618	47	−11.230212	50	−11.228501
9	−11.170617	17	−11.230226	19	−11.228515
10	−11.148964	42	−11.230196	44	−11.228487
11	−11.157261	70	−11.230190	53	−11.228481
12	−11.171696	39	−11.230223	39	−11.228512
13	−11.161546	66	−11.230223	46	−11.228506
14	−11.164816	33	−11.230176	29	−11.228485
15	−11.143458	32	−11.230226	31	−11.228515
16	−11.151136	54	−11.230208	45	−11.228498
17	−11.157329	33	−11.230206	41	−11.228498
18	−11.171771	41	−11.230190	48	−11.228481
19	−11.141685	39	−11.230206	40	−11.228495
20	−11.150264	35	−11.230202	38	−11.228492

The initial bond length was 0.72 Å.
[a] Unconstrained results are taken from Table I.
[b] Convergence criteria were a maximum gradient component of <0.00005 au and an energy change of $<10^{-7}$ hartree.

the intermolecular bonding, are superior to both **Z**-matrix and standard delocalized or natural internal coordinates. Using the Schmidt orthogonalization scheme introduced earlier,[4] and constraining all the *intramolecular* degrees of freedom, it is possible to carry out full rigid-body optimizations.

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