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Geometry Optimization Made Simple with Translation and Rotation Coordinates

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The effective description of molecular geometry is important for theoretical studies of intermolecular interactions. Here we introduce a new translation-rotation-internal coordinate system (TRIC) which explicitly includes the collective translations and rotations of molecules, or parts of molecules such as monomers or ligands, as degrees of freedom. The translations are described as the centroid position and the orientations are represented with the exponential map parameterization of quaternions. When TRIC is incorporated into geometry optimization calculations, the performance is consistently superior to existing coordinate systems for a diverse set of systems including water clusters, organic semiconductor donor-acceptor complexes, and small proteins, all of which are characterized by nontrivial intermolecular interactions. The method also introduces a new way to scan the molecular orientations while allowing orthogonal degrees of freedom to relax. Our findings indicate that an explicit description of molecular translation and rotation is a natural way to traverse the many-dimensional potential energy surface.

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1 I. INTRODUCTION

2 Intermolecular interactions are widely recognized for their central role in determining the
3 structure, function, and properties of macromolecules, molecular complexes, and molecu-
4 lar materials.¹⁻⁴ In theoretical chemistry, the fundamental tools for studying intermolecular
5 interactions include optimizing the molecular geometry to locate the critical points on the
6 many-dimensional potential energy surface, then calculating and characterizing the interac-
7 tions at a given geometry. In recent years, significant advances have been made toward the
8 second goal, such as accurate approximations to high-level electronic structure theories⁵⁻⁸
9 and energy decomposition analyses.⁹⁻¹⁵ However, achieving the first goal of efficiently opti-
10 mizing these molecular geometries is still challenging; this is because the potential energy
11 surface is relatively flat along the intermolecular directions compared to intramolecular ones,
12 and long sequences of energy and gradient evaluations are often required to reach a local
13 minimum. Geometry optimization methods that efficiently describe intermolecular degrees
14 of freedom may greatly accelerate these nontrivial calculations.

15 The Cartesian coordinate system is the simplest way to describe the molecular geometry
16 and is needed to carry out the energy and gradient evaluations. Because the potential energy
17 surface is highly nonlinear and coupled in the Cartesian coordinates (denoted as \mathbf{x}), only
18 small steps are possible in the downhill direction. Internal coordinates (ICs, denoted as \mathbf{q})
19 are functions of the Cartesian coordinates that better reflect the collective motions of the
20 atoms. ICs can describe displacements along curved pathways and decouple different kinds
21 of molecular displacements, allowing the optimization algorithm to take more efficient steps.
22 Given a displacement in the internal coordinates $\Delta\mathbf{q}$, the corresponding displacement in the
23 Cartesian coordinates $\Delta\mathbf{x}$ is computed as:

$$\Delta\mathbf{x} = \mathbf{B}^T \mathbf{G}^{-1} \Delta\mathbf{q}, \tag{1}$$

24 where \mathbf{B} is the Wilson B-matrix ($B_{ij} = \partial q_i / \partial x_j$) and $\mathbf{G} = \mathbf{B}\mathbf{B}^T$.¹⁶ When \mathbf{q} is a nonlinear
25 function, Equation 1 is applied iteratively until a desired IC displacement is achieved.

26 An early IC system is the Z-matrix coordinates^{17,18} where the position of an atom is
27 described using a distance, angle and/or dihedral angle with respect to other atoms; we will
28 refer to these individual functions as *primitive* ICs. The Z-matrix coordinates encounters
29 difficulties for cyclic systems where there are more ICs than Cartesian coordinates, which
30 makes \mathbf{G} ill-behaved; Pulay and Fogarasi showed that this can be overcome by using a

31 generalized inverse of \mathbf{G} .¹⁹ Schlegel extended this method by automatically constructing a
32 full set of primitive ICs from the connectivity graph of the molecule, which we refer to as the
33 redundant IC (RIC) system in this paper.²⁰ The generalized inverse of \mathbf{G}^{RIC} is expensive due
34 to the numerous primitive ICs. Baker proposed the delocalized internal coordinate system
35 (DLC) to remove the redundancies, where each delocalized coordinate is a linear combination
36 of primitive ICs corresponding to an eigenvector of \mathbf{G}^{RIC} with a nonzero eigenvalue.²¹⁻²³ As
37 a result, \mathbf{G}^{DLC} has a smaller dimension and is easier to invert.

38 When the above coordinate systems are applied to multiple molecules, the atoms be-
39 tween molecules are connected using a minimum spanning tree to describe the system as a
40 single “super-molecule”.²⁰ In this procedure, a minimal number of fictitious intermolecular
41 “bonds” are added to connect the molecules at the points of closest contact, which increases
42 the number of distances by the total number of molecules minus one; intermolecular angles
43 and dihedrals are then added in an analogous fashion to the single-molecule case. To avoid
44 introducing potentially ill-behaved primitive ICs between molecules, Baker proposed replac-
45 ing them with inverse interatomic distances, but an artificial cutoff is necessary to avoid
46 the number of interatomic distances increasing quadratically.^{24,25} Alternatively, Billeter and
47 Thiel introduced the hybrid delocalized internal coordinate (HDLC) method where the in-
48 termolecular displacements are described by adding all of the Cartesian coordinates into
49 the primitive IC set for the construction of delocalized ICs.²⁶ In the above methods, dis-
50 placements in the “intermolecular” primitive ICs will affect the inter- and intra-molecular
51 structures simultaneously. We hypothesize that a coordinate system that separately de-
52 scribes the inter- and intra-molecular degrees of freedom could improve the performance of
53 geometry optimizations.

54 The position of a molecule is easily described using its average Cartesian coordinates (i.e.
55 centroid), but describing the orientation is more challenging. First of all, a suitable definition
56 of rotation for non-rigid molecules is required. Second, an ideal representation of rotation
57 should be differentiable, such that the Wilson-B matrix can be evaluated analytically; non-
58 redundant, such that no additional constraints are needed in the parameter space; and free
59 of singularities. As the rotation group $\text{SO}(3)$ is three-dimensional, a non-redundant rotation
60 IC should have three independent variables. These criteria are not satisfied by most existing
61 rotation parameterizations, as will be discussed later.

62 In this paper, we introduce a well-behaved internal coordinate for molecular orientation,

63 which accounts for non-rigid molecules with the least-squares superposition method^{27–29}
 64 and uses the exponential map parameterization of rotations.³⁰ By including translation and
 65 rotation into the primitive IC set and applying the existing delocalization methods, it forms a
 66 new coordinate system that we refer to as translation-rotation-internal coordinates (TRIC).

67 The rest of the paper is organized as follows: We first provide mathematical details of
 68 the new translation and rotation coordinates, together with their derivative formulas. We
 69 demonstrate the improved efficiency of TRIC in geometry optimization applied to proto-
 70 typical systems compared to other coordinate systems. Finally, we show how TRIC enables
 71 constrained optimization in the molecular orientation, providing a new way to scan the
 72 potential energy surface along intermolecular degrees of freedom.

73 II. THEORY

74 To build the coordinate system, the atoms are first partitioned into subunits; this could
 75 be done automatically by connecting pairs of atoms that are closer than the sum of their
 76 covalent radii^{31,32}, although other divisions are possible.³³

77 For each subunit, we define three translation and three rotation internal coordinates. The
 78 translation internal coordinate is defined simply as the arithmetic average of the Cartesian
 79 coordinates:

$$\bar{x}_i = \frac{1}{N} \sum_{n=1}^N x_{in}; \quad i \in \{1, 2, 3\}. \quad (2)$$

80 where the notation x_{in} denotes the i -th Cartesian coordinate of the n -th atom. The deriva-
 81 tives are trivial to compute as $\partial \bar{x}_i / \partial x_{jn} = \delta_{ij} / N$.

82 Along similar lines, we seek a differentiable function $\mathbf{v}(\mathbf{x}, \mathbf{y})$ describing a rotation which
 83 brings an ordered list of Cartesian coordinates \mathbf{x} into maximum overlap with a reference \mathbf{y} ,
 84 which is set to the starting geometry. We shall assume without loss of generality that \mathbf{x} and
 85 \mathbf{y} have been shifted such that their centroids are located at the origin. The optimal rotation
 86 $\mathbf{v}(\mathbf{x}, \mathbf{y})$ minimizes the residual squared displacement $D(\mathbf{x}, \mathbf{y}; \mathbf{v}')$ as:

$$\mathbf{v}(\mathbf{x}, \mathbf{y}) = \operatorname{argmin}_{\mathbf{v}'} D(\mathbf{x}, \mathbf{y}; \mathbf{v}') = \operatorname{argmin}_{\mathbf{v}'} \frac{1}{N} \|\mathbf{U}(\mathbf{v}')\mathbf{x} - \mathbf{y}\|^2, \quad (3)$$

87 where $\mathbf{U}(\mathbf{v}')$ is a 3×3 rotation matrix parameterized by \mathbf{v}' and $\|\cdot\|$ is the Euclidean norm.

88 The trivial representation is to use the elements of \mathbf{U} themselves, but there are nine
 89 elements which makes it redundant. The Euler angle representation has the correct number

90 of parameters, but suffers from singularities when two of the rotation axes are parallel. A
 91 third representation is the rotation quaternion: for a rotation through angle θ around the
 92 axis defined by a unit vector (u_x, u_y, u_z) , the corresponding quaternion is defined as

$$\mathbf{q} = (q_0, q_1, q_2, q_3) = \left(\cos \frac{\theta}{2}, u_x \sin \frac{\theta}{2}, u_y \sin \frac{\theta}{2}, u_z \sin \frac{\theta}{2} \right) \quad (4)$$

93 and $U(\mathbf{q})$ is given in Eq. 33 of Ref. 28. In this paper, all vectors (such as \mathbf{u}) are defined in
 94 the global frame, as we do not use molecule-specific local frames.

95 Following the derivation of Coutsiaris and coworkers,²⁸ Equation 3 may be written in terms
 96 of quaternions using ordinary linear algebra as

$$\mathbf{q}(\mathbf{x}, \mathbf{y}) = \operatorname{argmin}_{\mathbf{q}'} D(\mathbf{x}, \mathbf{y}; \mathbf{q}') = \operatorname{argmin}_{\mathbf{q}'} \frac{1}{N} (|\mathbf{x}|^2 + |\mathbf{y}|^2 - 2\mathbf{q}'^T \mathbf{F} \mathbf{q}') \quad (5)$$

97 where \mathbf{F} is the symmetric matrix given by

$$\mathbf{F} = \begin{pmatrix} R_{11} + R_{22} + R_{33} & R_{23} - R_{32} & R_{31} - R_{13} & R_{12} - R_{21} \\ R_{23} - R_{32} & R_{11} - R_{22} - R_{33} & R_{12} + R_{21} & R_{13} + R_{31} \\ R_{31} - R_{13} & R_{12} + R_{21} & -R_{11} + R_{22} - R_{33} & R_{23} + R_{32} \\ R_{12} - R_{21} & R_{13} + R_{31} & R_{23} + R_{32} & -R_{11} - R_{22} + R_{33} \end{pmatrix} \quad (6)$$

98 and \mathbf{R} is calculated from the Cartesian coordinates as

$$R_{ij} = \sum_{n=1}^N x_{in} y_{jn}, \quad i, j = 1, 2, 3. \quad (7)$$

99 In Equation 5, D is minimized when the quadratic form $\mathbf{q}'^T \mathbf{F} \mathbf{q}'$ is maximized. Thus the
 100 optimal rotation quaternion \mathbf{q} is the eigenvector corresponding to the largest eigenvalue of
 101 \mathbf{F} .

102 The quaternion representation is free of singularities, but it contains four variables which
 103 makes it redundant. Another closely related parameterization that overcomes this problem
 104 is the exponential map, which is defined as

$$v_i = 2q_i \left(\frac{\cos^{-1}(q_0)}{\sqrt{1 - q_0^2}} \right); \quad i = 1, 2, 3, \quad (8)$$

105 where \mathbf{v} describes a rotation of $|\mathbf{v}|$ radians about the axis $\hat{\mathbf{v}}$; thus the magnitude and axis
 106 of rotation are encoded into a single three-dimensional vector. We note in passing that the
 107 exponential map is very closely related to the *axis-angle* representation of rotations.

108 A well-known fact about the rotation group $SO(3)$ is that it cannot be mapped into
 109 \mathbb{R}^3 without singularities.³⁰ In the case of the exponential map, the singularities in \mathbb{R}^3 are
 110 spherical surfaces with radius $2n\pi$ where n is a positive integer; this is because these vectors
 111 correspond to n complete revolutions which leave the coordinates unchanged. Moreover,
 112 any rotation with a larger norm than π is equivalent to a smaller rotation in the opposite
 113 direction. In practice, we detect when $|\mathbf{v}|$ exceeds 0.9π and reset the reference positions \mathbf{y} ,
 114 and this effectively avoids all such singularities. Therefore, the exponential map is suitable
 115 as the rotational internal coordinate.

116 The partial derivatives $\partial v_i/\partial x_{nj}$ are needed to compute the Wilson B-matrix. First note
 117 that the derivative of the exponential map parameters in terms of the quaternion elements
 118 are given by:

$$\begin{aligned} \frac{\partial v_i}{\partial q_0} &= q_i \left(2 \frac{q_0 \cos^{-1}(q_0)}{(1 - q_0^2)^{\frac{3}{2}}} - \frac{2}{(1 - q_0^2)} \right); \\ \frac{\partial v_i}{\partial q_i} &= q_0. \end{aligned} \quad (9)$$

119 In the neighborhood of $q_0 \rightarrow 1$ corresponding to vanishingly small rotations, Equations 8
 120 and 9 cannot be used because the numerator and denominator both vanish. This can be
 121 addressed by taking the Taylor expansion of Equation 8 around $q_0 = 1$, and the expressions
 122 simplify to:

$$v_i = 2 - \frac{2}{3}(q_0 - 1); \quad (10)$$

$$\frac{\partial v_i}{\partial q_0} = -\frac{2}{3}q_i; \quad \frac{\partial v_i}{\partial q_i} = q_0, \quad (11)$$

124 thus allowing us to compute the exponential map and its derivatives in the entire region of
 125 interest including the origin. By the chain rule, the desired derivative formula is given by

$$\partial v_i/\partial x_{nj} = \sum_{k=1}^4 \partial v_i/\partial q_k \times \partial q_k/\partial x_{nj} \text{ with the first term given by Equations 9 and 11 above.}$$

127 The quaternion derivative $\partial \mathbf{q}/\partial x_{nj}$ is given by the derivative formula for the eigenvector
 128 of a matrix:³⁴

$$\frac{\partial \mathbf{q}}{\partial x_{jn}} = (\lambda \mathbf{I} - \mathbf{F})^+ \frac{\partial \mathbf{F}}{\partial x_{jn}} \mathbf{q}, \quad (12)$$

129 where $(\cdot)^+$ is the generalized matrix inverse, λ is the largest eigenvalue of \mathbf{F} given by Equa-
 130 tion 6 above, and \mathbf{q} is the corresponding eigenvector. The derivatives $\partial \mathbf{F}/\partial x_{nj}$ are linear
 131 combinations of derivatives of \mathbf{R} , for example:

$$\frac{\partial F_{11}}{\partial x_{jn}} = \frac{\partial R_{11}}{\partial x_{jn}} + \frac{\partial R_{22}}{\partial x_{jn}} + \frac{\partial R_{33}}{\partial x_{jn}} \quad (13)$$

132 where

$$\frac{\partial R_{ij}}{\partial x_{kn}} = \delta_{ik}y_{jn}. \quad (14)$$

133 III. COMPUTATIONAL METHODS

134 We developed GeomeTRIC, an open-source optimization program that interfaces to quan-
135 tum chemistry software by passing Cartesian coordinates as input and retrieving the output
136 energies and Cartesian gradients (see Supporting Information). GeomeTRIC implements
137 Cartesian coordinates, redundant IC (RIC), delocalized IC (DLC), hybrid DLC (HDLC),
138 and translation-rotation-internal coordinates (TRIC). The Q-Chem 4.2 software package³⁵
139 was used for the water clusters, and the TeraChem software package³⁶⁻³⁸ was used for the
140 others. The details of the optimization algorithm are given in the Supporting Information;
141 we chose a force constant of 0.05 a.u. for the translation and rotation coordinates when
142 constructing the initial guess Hessian matrix.

143 IV. RESULTS AND DISCUSSION

144 **Copper phthalocyanine (CuPc) and C₆₀** are a donor/acceptor pair of materials
145 that are extensively studied as a model system for organic photovoltaics. The molecular
146 packing at the interface in thin films and bulk heterojunctions depends heavily on the
147 intermolecular interactions, and in turn influence the optical and electronic properties.⁴³ In
148 this example calculation, 23 starting structures were randomly selected from a molecular
149 dynamics simulation of a CuPc/C₆₀ mixture which uses the UFF force field⁴⁴.

150 Figure 1 shows the impact of the coordinate system on the optimization results in a
151 representative example. The optimization using TRIC converges in 248 cycles, followed
152 by HDLC (322), DLC (413), RIC (420) and Cartesians (771). Moreover, the primitive
153 coordinates describing intermolecular motion affects the path taken by the optimization
154 and the final geometry. TRIC is the only coordinate system to contain the translation and
155 rotation coordinates, and converges to a stacked CuPc dimer with C₆₀ molecules in close
156 contact. The HDLC / Cartesian coordinates both use the atomic Cartesian coordinates,
157 and they converge to two similar structures (RMSD = 0.40 Å) where the CuPc molecules
158 are far apart. The RIC/DLC both use interatomic distances, angles, and dihedral angles,

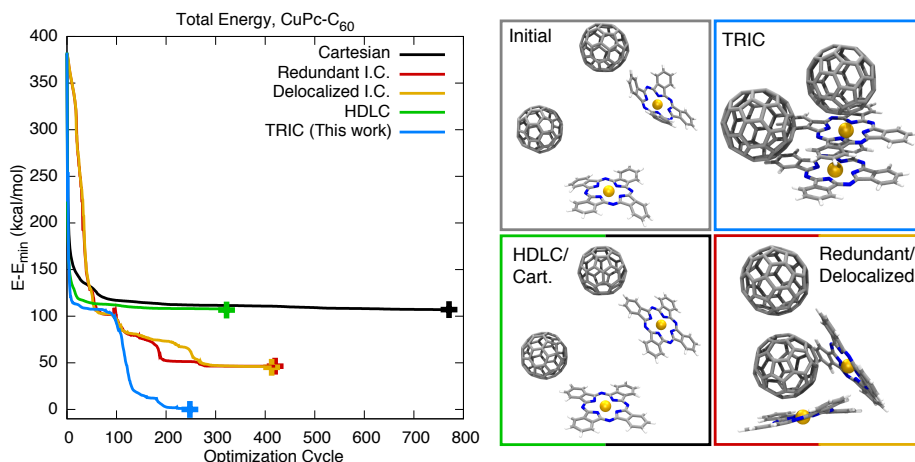


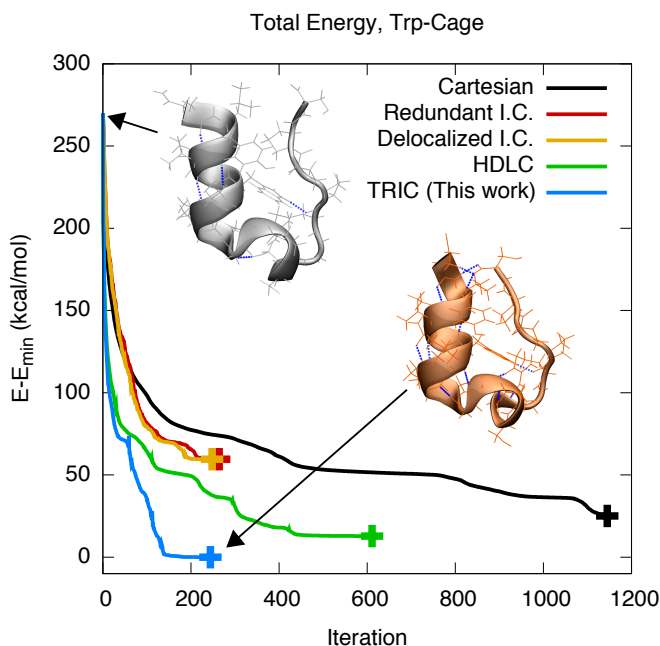
FIG. 1. Optimization results for $2\text{CuPc}-2\text{C}_{60}$ (neutral, triplet) using different choices of the coordinate system. Calculations used the PBE0 approximation³⁹ with the DFT-D3 empirical dispersion correction⁴⁰, the LANL2DZ basis set and effective core potential^{41,42} for copper, and the 3-21G basis for all other atoms. Energies are referenced to the TRIC-optimized structure which has the lowest energy. The lower panels show initial and optimized structures under different coordinate systems. The HDLC/Cartesian coordinates and RIC/DLC converged to highly similar structures (RMSD < 1.5 Å) so only one structure is shown for each pair. Atoms are colored as C, gray; N, blue; Cu, orange.

159 and they also converge to two similar structures (RMSD = 1.62 Å) where the two CuPc
 160 molecules are perpendicular.

161 It is well-known that the result of a local optimization largely depends on the choice
 162 of initial conditions, and even a small perturbation of the starting structure could cause
 163 convergence to a different minimum. Thus, we tested TRIC, HDLC and DLC on the full set
 164 of 23 starting structures to assess the statistical significance of the results generated using
 165 these coordinate systems. Figure S1 shows that the HDLC calculations have the largest
 166 number of cycles (428 ± 231); DLC converges in fewer iterations (250 ± 104) and TRIC
 167 requires the least (216 ± 64). All of the TRIC calculations converged in fewer than 400
 168 cycles, and 15 out of 23 calculations reached a lower final energy than either HDLC or DLC.
 169 Student's t-test indicates that TRIC converges to the lowest energy structure more often
 170 than HDLC or DLC with a 95% confidence level.

171 **Trp-cage Miniprotein.** Proteins are diverse polymers with complex nonbonded in-

172 teractions; the monomers are covalently bonded through the protein backbone and possess
 173 flexible side chains, making this an interesting case study for internal coordinate systems.
 174 Here we minimized the energy of the Trp-cage miniprotein, starting from the solution NMR
 175 structure, PDB ID 1L2Y.⁴⁵ The protein was divided into subunits according to the amino
 176 acid residue number.



177

178 FIG. 2. Optimization results for Trp-cage, using the same electronic structure method as CuPc-
 179 C60 but with the COSMO continuum solvent model added.^{46,47} The protein backbone is shown
 180 as ribbons and atoms are shown as lines; hydrogen bonds are highlighted in blue with a 3.0 Å
 181 distance cutoff between heavy atoms and a 30 degree cutoff for the angle between hydrogen, donor
 182 atom and acceptor atom.

183 Figure 2 shows the optimization results; TRIC converges in the fewest iterations (244),
 184 followed by DLC (248), RIC (264), HDLC (634) and Cartesian (1146). Here, both TRIC
 185 and HDLC include the bonds, angles, and dihedrals between residues. The TRIC optimized
 186 structure has a heavy-atom RMSD of 1.94 Å from the starting structure and contains more
 187 hydrogen bonds, in line with our expectation that the energy minimum should contain more
 188 hydrogen bonds than a structure obtained at room temperature. The DLC and redundant
 189 IC behave almost identically and converge to a pair of highly similar structures (RMSD <

190 0.01 Å). Finally, the HDLC and Cartesian coordinates converge in a much greater number
191 of iterations (> 600) and the two final structures are rather similar (RMSD = 0.60 Å).

192 The amino acid residues in a protein are connected by the backbone amide bonds, thus
193 removing these bonds from the connectivity graph will disconnect the protein into separate
194 fragments. This in turn prevents the primitive ICs involving atoms on different residues
195 from being generated and leads to a block-diagonal \mathbf{G} matrix, which is suggested in Ref. 26
196 to speed up the inverse iterations for Cartesian steps. Figure S2 shows that excluding these
197 bonded ICs increases the number of optimization cycles for TRIC by a greater amount than
198 for HDLC, although TRIC still converges in fewer cycles in both cases. This is also observed
199 statistically for all 38 NMR structures using the AMBER99-SB force field⁴⁸ in Figure S3.
200 Thus, although TRIC is designed to reduce the number of optimization cycles, decoupling
201 residues from each other is one way to accelerate the inverse iterations when they are a
202 computational bottleneck.

203 **Water clusters** contain strong but flexible hydrogen bonds, which leads to a rich di-
204 versity of local minimum structures for water clusters as small as the hexamer.⁴⁹ We thus
205 examined the influence of the coordinate system on the distribution of optimization results
206 for a large number of water cluster structures drawn from liquid molecular dynamics simu-
207 lations using the iAMOEBA model⁵⁰. Five cluster sizes were considered (6, 8, 12, 16, and 20
208 molecules) with 100 structures each. We also present comparisons of our results with other
209 software packages, including DL-FIND⁵¹ (using HDLC) and Q-Chem 4.2³⁵ (using DLC) in
210 Figure S4.

211 Figure 3 compares the performance of different coordinate systems for optimizing 12 water
212 molecules. The number of optimization cycles is significantly different between coordinate
213 systems, while the distribution of final energies are quite similar. The calculations with
214 TRIC have the smallest mean and variance in the number of cycles compared to the other
215 coordinate systems. Although the Cartesian coordinates are peaked at the largest num-
216 ber of iterations, DLC has the largest number of outliers requiring more than 500 cycles.
217 These outliers could indicate the risks of using interatomic distances, angles and torsions
218 to describe intermolecular degrees of freedom, as they undergo very different motions from
219 intramolecular ones.

220 Figure 4 shows how the number of optimization cycles depends on the system size. TRIC
221 is the most efficient for all of the system sizes tested, and also has the lowest slope of 4.1,

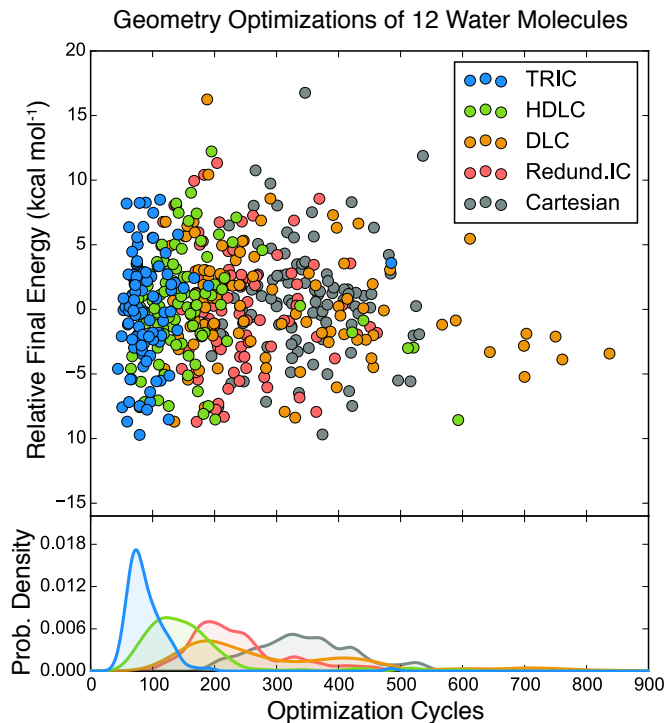


FIG. 3. Optimization results for 100 water clusters (12 molecules) with five different coordinate systems. The PBE0-D3 approximation and 6-31G* basis were used. The scatter plot shows the number of optimization cycles vs. the final minimized energies relative to the average. The lower panel is a kernel density estimate with kernel width 0.2 showing the distribution of optimization cycles for each coordinate system.

222 indicating the increase in the number of cycles per molecule added. At the largest cluster
 223 sizes (20 and 24), the slope decreases to 2.3 cycles per molecule added; the apparent sub-
 224 linear scaling of the cycle number is encouraging considering the scaling of the electronic
 225 structure method is often quadratic or greater. Taken together with the CuPc-C₆₀ and Trp-
 226 cage results, the data indicates that TRIC significantly reduces the cost of intermolecular
 227 geometry optimization.

228 A. Orientation constrained optimization

229 The TRIC coordinates enable a new kind of constrained optimization where the relative
 230 orientations of molecules are constrained while allowing the orthogonal degrees of freedom
 231 to relax, which is useful for characterizing the intermolecular potential energy surface. To

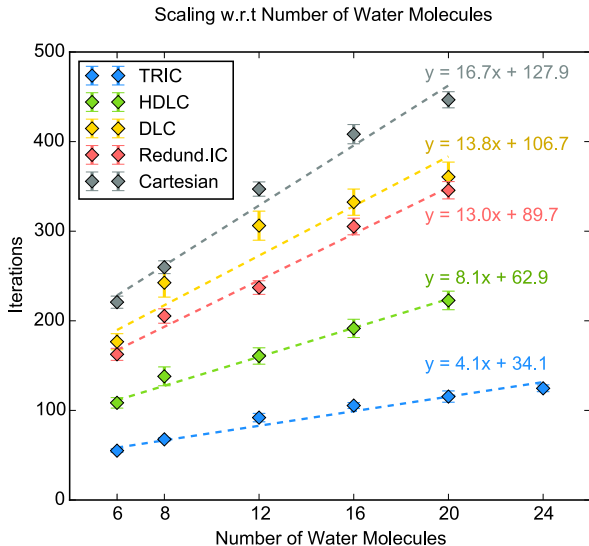


FIG. 4. Scaling behavior of the number of optimization cycles with respect to the cluster size. The error bars are one standard error. The dotted lines are linear fits.

232 demonstrate this capability we carried out orientation-constrained optimizations on a pen-
 233 tacene dimer, where one molecule is held to its original orientation while rotating the other
 234 around the chosen axis. The constraints are implemented using Lagrange multipliers as
 235 described in Ref. 52.

236 Although the idea of constraining the molecular orientation is intuitive, care must be
 237 taken to select the correct internal coordinates to constrain. Because the energy of the
 238 overall system is invariant to overall rotations, we fix the orientation of one pentacene
 239 molecule relative to its original structure and scan the orientation of the other molecule.
 240 The rotation is specified using a rotation axis and a rotation angle; the optimization then
 241 searches for a geometry where the molecule is rotated by the specified angle with respect to
 242 the starting structure. By scaling the unit vector of the specified rotation axis by the specified
 243 angle, one obtains the constraint values for the exponential map parameters corresponding
 244 to v_i in Equation 8.

245 Figure 5 shows a sequence of optimized structures of the pentacene dimer as the second
 246 molecule is rotated through 180 degrees in 5 degree increments. We scanned the orientation
 247 first with dispersion-corrected PBE0^{39,40} and then with the GAFF force field.⁵³, and the
 248 results are significantly different. The final structure in DFT has a much smaller horizontal
 249 offset compared to the force field, which indicates stronger intermolecular interactions in

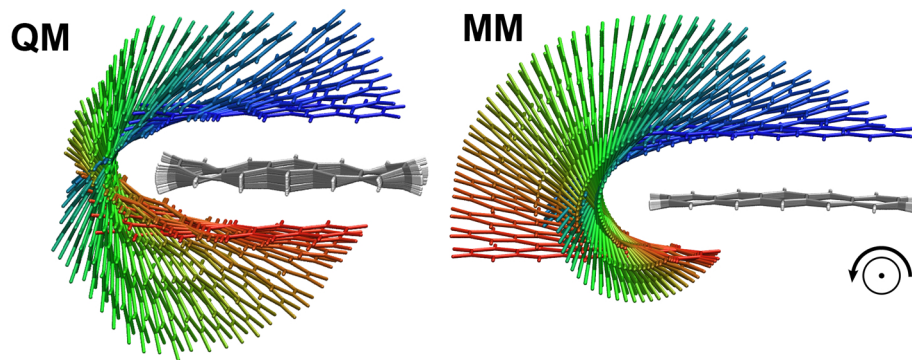


FIG. 5. Optimized structures of pentacene dimer using PBE0-D3/6-311++G(d,p) (top) and the GAFF force field (bottom). The rotation axis is perpendicular to the plane of the image. The structures are aligned using the monomer in gray/white as a reference, and the other monomer is colored according to sequence number (blue, initial; red, final). The details of this calculation are provided in the Supporting Information.

250 DFT. DFT also predicts much greater distortions in the monomers, which could arise from
 251 the relatively strong intermolecular interactions, or could indicate that molecules are less
 252 rigid. The stronger interactions are also evident in Figure S5, which shows that DFT predicts
 253 much higher energy barriers to rotation.

254 Relaxed potential energy scans are a commonly used approach in theoretical chemistry,
 255 principally as a means for testing hypothetical reaction coordinates.^{54–56} With the introduc-
 256 tion of the rotational coordinate in TRIC, it is now possible to perform a relaxed potential
 257 energy scan over the molecular orientation. We conjecture that this could open up new di-
 258 rections in the study of intermolecular forces, particularly concerning the interplay between
 259 molecular distortions and intermolecular forces that have been proposed for inclusion into
 260 polarizable force fields.⁵⁷

261 V. CONCLUSION

262 As electronic structure theory is increasingly applied to study intermolecular interac-
 263 tions, corresponding advances in geometry optimization methods are essential. The TRIC
 264 coordinate system significantly reduces the number of optimization cycles needed for these
 265 complicated systems and also enables exploring the potential energy surface while con-

266 straining the intermolecular orientations. Such calculations can provide valuable data for
267 parameterizing empirical potentials which sample the intermolecular degrees of freedom in
268 finite-temperature simulations.⁵⁸ We are optimistic that further applications of TRIC will
269 include basin-hopping^{33,59,60} and reaction path-finding methods⁶¹⁻⁶⁷ as they all involve ge-
270 ometry optimizations on molecular potential energy surfaces.

271 VI. ACKNOWLEDGEMENTS

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276 VII. SUPPORTING INFORMATION

277 Supporting Information Available. The open-source code that implements TRIC is avail-
278 able online at <https://github.com/leeping/geomeTRIC>.

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