Zusammenfassung Literaturrecherche Nomodecopaper

Abkürzungen:

- NMA (Normal Mode Analysis)
- MWC (Mass weighted cartesian coordnates)

Redundant internal coordinates, compliance constants and non-bonded interactions – some new insights

MOUMITA MAJUMDER and SADASIVAM MANOGARAN

https://doi.org/10.1007/s12039-012-0357-7

> Identifying internal coordinates when only cartesian cordinates, masses and force constants are given.

NMA in MWC --> normal modes tell us ICs that are needed --> chosen properly **minimum mixing**.

Results:

Stretching relaxed force constantes of bonds are suitable to characterize the bond order of hydrogen bond

Optimization of Strong and Weak Coordinates

MARCEL SWART, F. MATTHIAS BICKELHAUPT

https://doi.org/10.1002/qua.21049

> Geometry Optimization of equilibrium and transition state structures for strong and weak coordinates, screening function to differentiate strong and weak coordinates

Choice of primitives ICs to generate natural ICs is a matter of "hand work

Using delocalized coordinates approach by Baker

$\Delta q = w_p B \Delta x$, w_p diagonal matrix with weight function for primitive IC

Diagonalization of $G = B_p B_p^T$

Gives $G(UR) = UR\begin{pmatrix} \Lambda \ 0 \ 0 \ 0 \end{pmatrix}$

Transform B matix in delocalized space $B_d = U^TB_d$

> Delocalized coordinates work well for strong coordinates, not designed for weak intermolecular coordinates

Degree of covalance (used in Nomodeco)

$p_{ij} = \exp[-(r_{ij}/C_{ij})-1]$

- r_{ij} distance
- C_{ij} sum of covalent radi
- around one for atoms covalently bonded, lower for weaker coordinates

Results

Geometry optimization in delocalized internals using weak and strong coordinates.

TABLE II

Number of geometry cycles for optimizing the geometry of systems involving weak coordinates with our geometry optimization scheme.*

Molecule	Iterations	Molecule	Iterations
$Ar\cdots Ar$	7	$H_2O\cdots H_3O^+$	40
$CH_4\cdots CH_4$	8	$H_2O\cdots NH_3$	13
$CH_4\cdots NH_3$	9	$H_2O\cdots NH_4^+$	22
$F^-\cdots HF$	6	$HF\cdots H_2O$	11
$H_2O\cdots H_2O$	11	$NH_3\cdots NH_3$	20
$Cyt\cdots Cyt$ (CC3)	16[a]	$CHBr_3\cdots H_2O_2$	29

* PW91/TZ2P results.
[a] BP86/DZP result.

The efficient optimization of molecular geometries using redundant internal coordinates

Vebjørn Bakken and Trygve Helgaker

Optimization of molecular geometries is discussed. Extra-redundant internal coordinates reduce the number of geometry steps, complete expressions for first and second derivatives of B matrix are presented

- Covalent bonds as well as hydrogen bonds are used

Transformation between cartesian and redundant

Gradient and hessian:

- $g_x = B^t g_q$

- $H_x = B^t H_q B + K$

where K is

$K_{jk} = \sum_{i}[g_q]i\,B'\{ijk\}$

Applying generalized inverse one can to the back transformation

- $g_q = (B^t)^+ g_x$
- $H_q = (B^t)^+(H_x - K)B^+$

TABLE X. The most efficient method of this work compared with results from the literature.

Molecule	STO-3G basis				6-31G* basis
	This work	Eckert *et al.* (Ref. 3)	Lindh *et al.* (Ref. 2)	Baker (Ref. 9)	This work
Water	4	4	4	6	5
Ammonia	5	6	5	6	5
Ethane	3	4	4	5	4
Acetylene	4	6	5	6	4
Allene	4	4	5	5	5
Hydroxysulphane	7	7	8	8	6
Benzene	3	3	3	4	3
Methylamine	4	5	5	6	5
Ethanol	4	5	5	6	5
Acetone	4	5	5	6	4
Disilyl ether	8	9	11	8	11
1,3,5-trisilacyclohexane	9	6	8	8	8
Benzaldehyde	4	5	5	6	5
1,3-difluorobenzene	4	5	5	5	5
1,3,5-trifluorobenzene	4	4	4	5	5
Neopentane	4	4	5	5	4
Furan	5	6	7	8	5
Naphtalene	5	6	6	5	5
1,5-difluoronaphtalene	5	6	6	6	5
2-hydroxybicyclopentane	9	9[a]	10	15	9
ACHTAR10	8	9	8	12	9
ACANIL01	7	8	8	8	6
Benzidine	9	7	10	9	9
Pterin	8	9	9	10	9
Difuropyrazine	6	7	7	9	7
Mesityl oxide	5	6	6	7	5
Histidine	16	14	20	19	16
Dimethylpentane	9	10	10	12	9
Caffeine	6	7	7	12	7
Menthone	12	10	14	13	13
Sum	185	196	215	240	198

[a]This molecule did not converge to the correct stationary point.

Results

Minimization extra-redundant systems should be used optimization is efficiently carried out.

The Choice of Internal Coordinates in Complex Chemical Systems

KÁROLY NÉMETH, MATT CHALLACOMBE, MICHEL VAN VEENENDAAL

https://doi.org/10.1002/jcc.21494

> Article talks about appropiate choice in internal coordinates in complex chmical systems.

> "Blackbox recognition of internal coordinates is fundamental for the extension of internal coordinate algorithms"

G Matrix connects B matrix with its pseudoinverse:

$G_c = B^T B$, $A = G_c^{-1}B^T$

G matrix has $N_f = 3N-6(5)$ nonzero eigenvalues, six zero eigenvalues for translations and rotations

Alternative Coordinate Selection Algorithms (Maybe to test in the future)

Selection based on Condition number of G_c.

1. Calculate λ_{max} and λ_{min}
2. Let $\lambda_c = |\lambda_{max}|/|\lambda_{min}|$
3. Condition number tells us how "pertubation" affects equation $Ax =b$
4. If condition number near 1 "well conditioned"
5. ICs give homogeneous description of space

Selection based on Cholesky Factorization of G_c?

Conectivity analysis --> **The von Arnim-Ahlrichs Approach**

Results

> New selection algorithms for ICs are presented wich recognize the coordinates for topologically complex systems.

Efficient Geometry Optimization of Molecular Clusters

JON BAKER, PETER PULAY

https://doi.org/10.1002/(SICI)1096-987X(20000115)21:1

> Using valence coordinates (stretches, bends, and torsions) to describe intramolecular degrees of freedom with inverse distance coordinates for intermolecular degrees of freedom, efficient set of coordinates can be derived for geom opt of molecular clusters.

"The efficient optimization of the geometries of weakly bound molecular clusters is a difficult task"

Again delocalized internal ICs are used $G = BB^T$

$G(UR) = UR\begin{pmatrix} \Lambda \ 0 \ 0 \ 0 \end{pmatrix}$

The all stretches, bends, torsions are generated based on atomic connectivity and all inverse distances between atoms of different molecules in clusters

for example $(H_2O)_{10}$:

- two $O-H$ stretches and one $\angle HOH$ bend for each molecule

- 405 additonal inverse distances, cutoffs are used!

Results:

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.

> Delocalized cluster coordinates where intermolecular bonding are represented with inverse distances are efficient at optimizing geometries of weakly bound molecular clusters

Polyatomic molecular potential energy surfaces by interpolation in local internal coordinates

Keiran C. Thompson ,Meredith J. T. Jordan, and Michael A. Collins

https://doi.org/10.1063/1.476259

> Method for expression of a PES for polyatomic molecules as interpolation of local Taylor expansions in internal coordinates is presented.

Redundant coordinate problem:

> For more than four atoms the number of bond lenghts is greated than the number of ICs $3N-6$ in any given region of the configuration space only a subset can form independent variables

All coordinates elements of vector space isomorphic to R^m, positions of atoms are described by R^3, set of all positions is R^{3N} mapping which constructs $N(N-1)/2$ bonds from $3N$ positions is non linear no vector space but a **Riemannian manifold**

The Jacobian, B has rank $3N-6$ there are six directions in R^{3N} which cannot be described using bond lengths

$$\frac{\partial V}{\partial X_n}\bigg|_{\mathbf{X}(i)} = \sum_{k=1}^{3N-6} \frac{\partial \zeta_k}{\partial X_n} \frac{\partial V}{\partial \zeta_k}\bigg|_{\zeta(i)} , \tag{4.1a}$$

$$\frac{\partial^2 V}{\partial X_n \partial X_m}\bigg|_{\mathbf{X}(i)} = \sum_{k=1}^{3N-6}\sum_{j=1}^{3N-6} \frac{\partial \zeta_k}{\partial X_n} \frac{\partial \zeta_j}{\partial X_m} \frac{\partial^2 V}{\partial \zeta_k \partial \zeta_j}\bigg|_{\zeta(i)}$$

$$+ \sum_{k=1}^{3N-6} \frac{\partial^2 \zeta_k}{\partial X_n \partial X_m} \frac{\partial V}{\partial \zeta_k}\bigg|_{\zeta(i)} . \tag{4.1b}$$

Expansion Potential energy using ICs, Problem numericall instability for example if a near planar configuration is seen.

Intrinsic Frequency Analysis of the Generalized Normal-Mode Vibrations for the Reaction H2 + CH3 —> H + CH4

Jerry A. Boatz and Mark S. Gordon

https://doi.org/10.1021/j100352a025

> Vibrational energy distributions and intrinsic frequencies are computed at selected points along the $H_2 + CH_3 \to H + CH_4$ intrinsic reaction coordinate at UHF/STO-3G level. Intrinsic frequencies provide evolution of generalized normal coordinates along the reaction path.
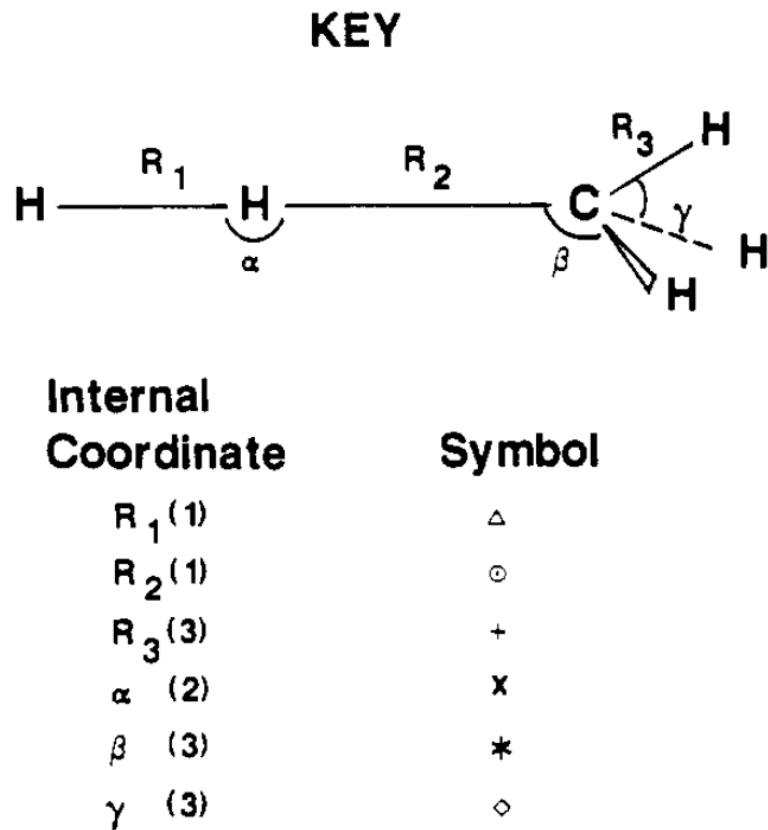
KEY

Figure 1. Symbol scheme used in Figures 3, 5, and 6. The number of symmetrically equivalent coordinates for each internal parameter is given in parentheses.

$f_{ij} = \partial^2 E / \partial x_i \partial x_j$ in cartesian

$F_{ij} = \partial^2 E / \partial r_i \partial r_j$ in internals

Diagonalization of f matrix

$\Lambda = l^t f l = D^t F D$ with $D = Bl$

Vibrational density matrix

$P_{mn}^i = D_{mi}F_{mn}D_{ni}/\lambda_i$

Energy distribution matrix is obtained from P^i and gives fractional contribution of IC r_m to generalized normal coordinate

Intrinsic frequencies

$v_n = \sum_m \sum_i P_{mn}^i \lambda_i$

v_n represents total contribution of internal coordinate r_n to the normal-coodrinate frequencies. Is the frequency associated with the single motion of a internal coordinate r_n

The Role of Anharmonicity in Hydrogen-Bonded Systems: The Case of Water Clusters

Berhane Temelso and George C. Shields https://doi.org/10.1021/ct2003308

> Nature of vibrational anharmonicity has been exained for small water clusters using second order vibrational pertubation theory (VPT2) applied on MP2 potential energy surfaces. Intermolecular modes are substantially more anharmonic than the intramolecular modes
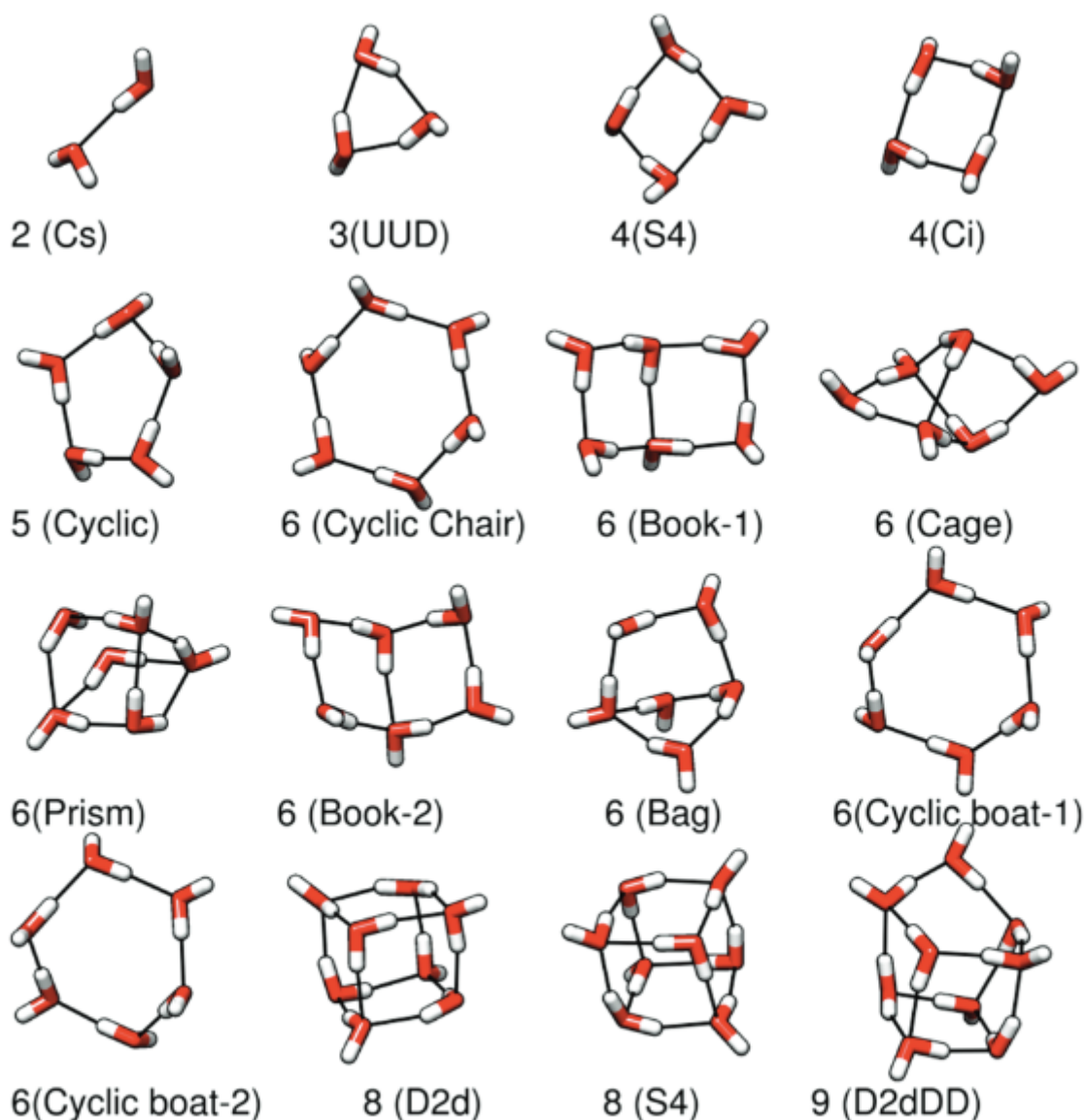

2 (Cs) 3(UUD) 4(S4) 4(Ci)

5 (Cyclic) 6 (Cyclic Chair) 6 (Book-1) 6 (Cage)

6(Prism) 6 (Book-2) 6 (Bag) 6(Cyclic boat-1)

6(Cyclic boat-2) 8 (D2d) 8 (S4) 9 (D2dDD)

Figure 1. The 16 water clusters included in this study.

- Each whater cluster has $2n$ high frequency intramolecular stretching modes
- n intramolecular bending modes
- $6n-6$ low frequency intermolecular modes

The vibration-rotation problem in triatomic molecules allowing for a large-amplitude bending vibration

J.T. Hougen, P.R. Bunker, J.W.C. Johns

https://doi.org/10.1016/0022-2852(70)90080-9

> Here the expression of the vibration-rotation Hamiltonian of a triatomic molecule are derived. Rectilinear displacment coordinates are inappropiate for vibrational motion in triatomic molecules when the amplitude of the bending is large.

Futher Theory / Stuff

Force Constants / Relaxed force Constants $V = V\_0 + G^T Z + \frac{1}{2}Z^T H Z + ...$

Z ... arbitrary displacement coordinate

Harmonic Potential $V = \frac{1}{2}Z^THZ$

Transition to internal coordinates: $V = \frac{1}{2}Q^T H\_q Q$

Hessian matrix $H\_q 0 \frac{\partial^2 V}{\partial Q\_i \partial Q\_j}$

Rather than internal displacement coordinates, an alternative approach to write the potential energy of a molecule as explained by Decius[12] is to write it as a quadratic form in terms of generalized displacement forces (negative gradient) G_q.

$$V = \frac{1}{2}{G_q}^T C G_q \text{ (eq. 5)}$$

This gradient G_q is the first derivative of the potential energy with respect to the displacement coordinates, which can be expressed as shown:

$$G_q = H_q Q \text{ (eq. 6)}$$

By substituting the expression of G_q in eq. 5 into equation 5, equation 7 is obtained.

$$V = \frac{1}{2}Q^T {H_q}^T C H_q Q \text{ (eq. 7)}$$

Thus, with the knowledge that H_q is positive definite, the only possible value of C which is the compliance matrix then must be:

$$C = {H_q}^{-1} \text{ (eq. 8)}$$

Relaxed force constants are inverse of diaognal C matrix element.

> While the force constant matrix F represents the rigitidy of a molecule, the compliance matrix G represents the flexibility of a molecule