Thermal Ellipsoid Analysis:

The Fossil Footprints of Restless Atoms

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I've been asking the same question for 35 years. What do our crystallographic anisotropic thermal-motion parameters mean? My approaches over the years include:

(1) **Visualizing anisotropic thermal motion** – a graphics program ORTEP (1965,1976,1996) illustrates thermal motion as fields of probability ellipsoids. Dr. Mike Burnett is now ORTEP's guardian and developer (email: ortep@ornl.gov).

(2) **Segmented-body thermal motion** – a program ORSBA (1967) combining Schomaker and Trueblood's rigid body and Busing and Levy's riding model to analyze molecular motion.

(3) **Higher-order thermal motion** – statistical models using a tensor cumulant expansion (1968) and a related Gram-Charlier expansion (1974) for crystallographic least-squares refinement.

(4) **Curvilinear thermal motion** – a mechanistic moment expansion which produces coefficients for the higher-order statistical models from rigid body libration parameters (1969).

(5) **Probability measures for thermal motion correlation** – a new exploratory approach utilizing the Radon-Nikodym density (derivative) for Gaussian probability measures and processes.

This lecture is on **correlated thermal motion** [items (1), (2) and (5)], and includes future research possibilities.

3n-Dimensional Mean-Square Thermal Motion in 3-Dimension Crystals

(n = Number of Atoms in Asymmetric Unit)

1. Stereoscopic **Thermal Ellipsoid Illustrations** – Visualization of certain types of correlated molecular motion, particularly large amplitude rigid-group libration and translation. Requires the viewer to have stereoscopic vision and chemical perception experience.

2. **Quantitative correlated-motion** analysis – based on large joint motion probability matrices derived from:

   (1) **Quantum mechanics** calculation of 3n-6 $\times$ 3n-6 mean-square displacement matrix for an isolated molecule, or 3n $\times$ 3n matrix for a small crystal structure.

   (2) Spectroscopic **normal coordinate analysis** assigning intramolecular symmetric displacement modes to molecular vibrational frequencies and intermolecular space-group symmetric lattice displacement modes to lattice vibration frequencies.

   (3) Starting with a set of m ($m \leq n$) 3×3 **crystallographic thermal-motion** matrices, one can use models such as the Schomaker-Trueblood rigid-body model to fill in some or all of the off-diagonal interatomic correlation blocks of the 3m $\times$ 3m matrix.

   (4) **Combinations** of (1), (2), and (3). Particularly recent work by Hans-Beat Bürgi of Switzerland, Bryan Craven of USA, and their coworkers.

Thermal Motion Attributes

True thermal motion components often seen in a small molecular crystal:

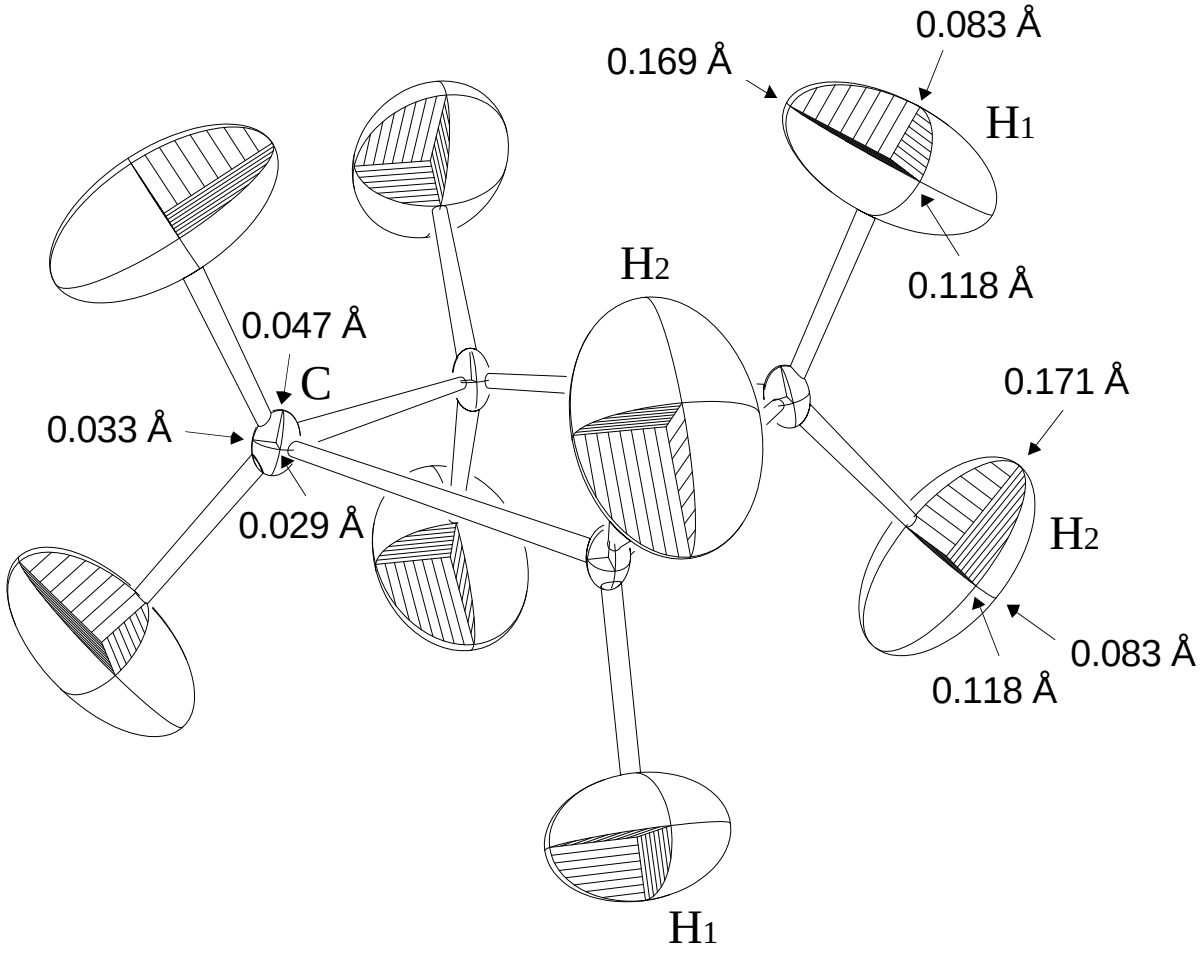
- Molecular rigid body motion
  - Translation
  - Libration
- Coupled rigid body motion
  - Phenyl group torsion
- Terminal group motion
  - H atom wag (neutron data)
  - Carbonyl O wag
  - Methyl torsion (neutron data)
  - Carboxyl oxygens torsion

Pathological effects that may make the thermal-motion pattern “look strange”:

- Crystal order and symmetry imperfections
  - Disorder at symmetry elements
  - General orientational disorder
- Poor data and/or refinement mistakes
  - Dick Harlow’s ORTEP-of-the-Year awards
- Wrong space group/unit cell mistakes
  - Dick Marsh’s “correction” awards

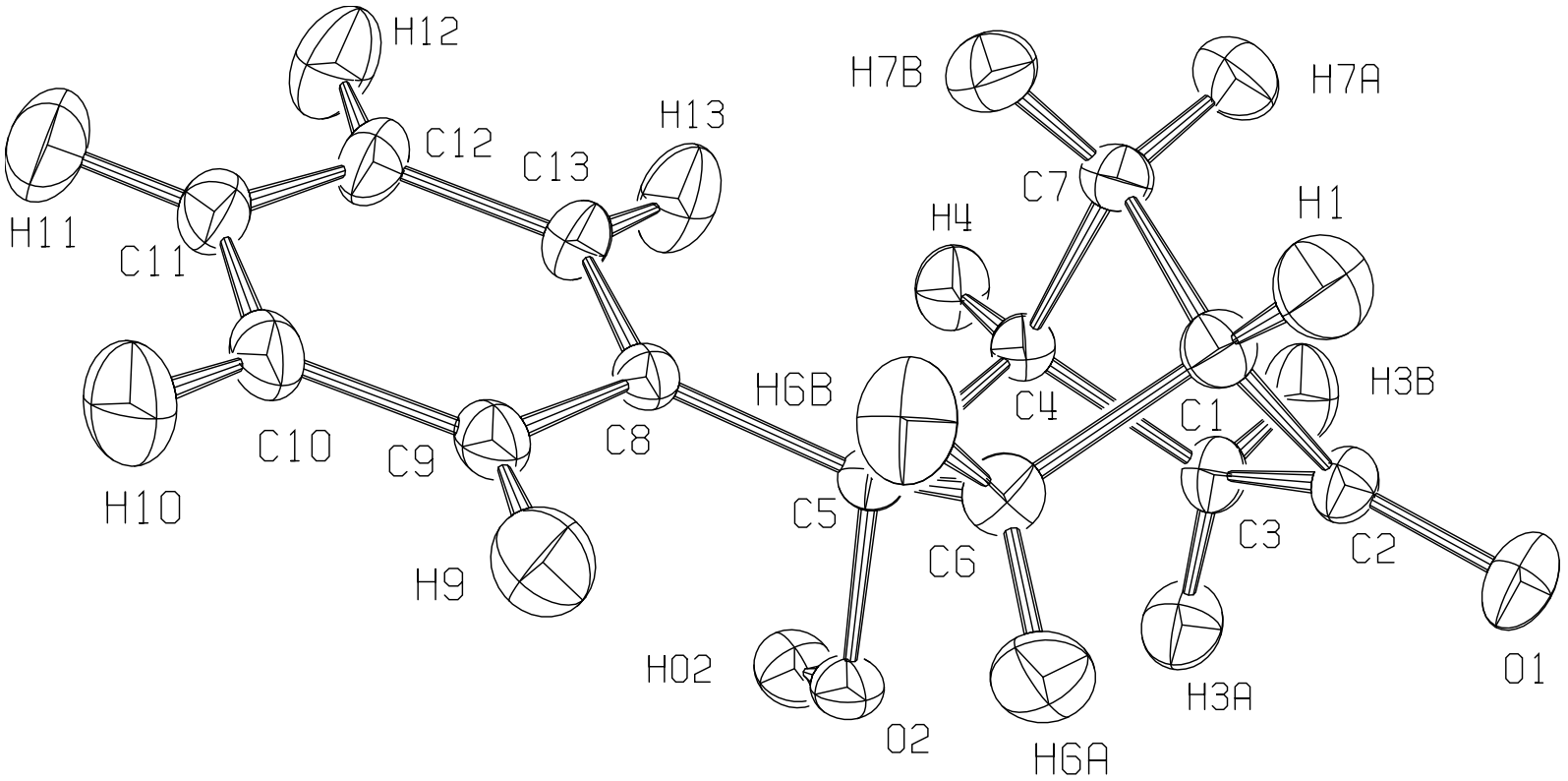
Internal Motion from Spectroscopic Normal Coordinate Analysis

Before fitting rigid body to organic structures derived through neutron diffraction, it is necessary to subtract out the internal motion using transferable parameters derived from molecular spectroscopy vibration frequencies. For benzene, the along-bond, in-plane, and out-of-plane rms displacements are (0.036Å, 0.029Å, 0.041Å) for C and (0.077Å, 0.116Å, 0.150Å) for H at 25° C. Related values for cyclobutane are illustrated below.



Visual Evaluation of ORTEP Drawings

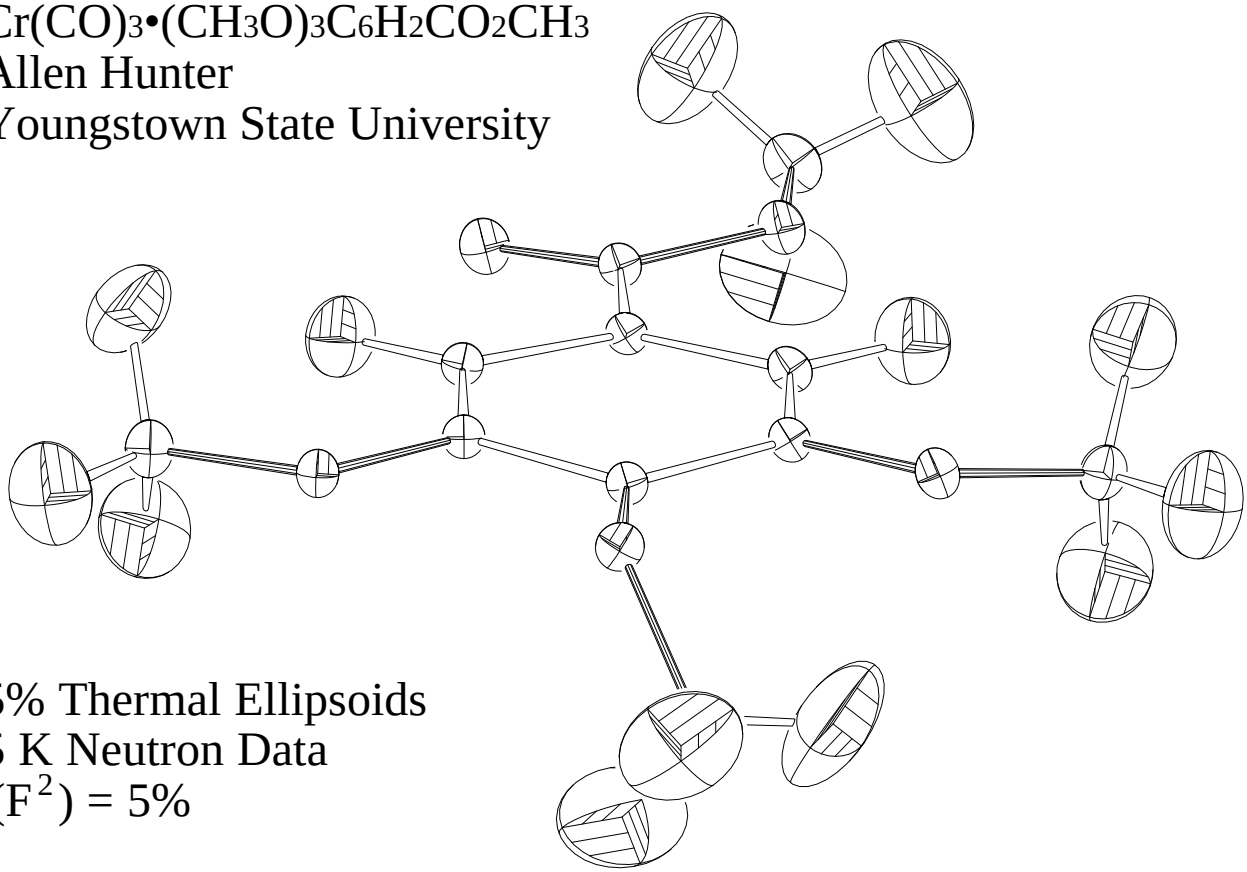
1. Check each peripheral atom for size and shape relative to its parent atom – should be larger and any shape differences should make chemical sense. (see C-H, C=O, O-H)
2. Check for reasonable torsion in terminal groups (CH_3, CO_2).
3. Check for rigid body motion in major groups and subgroups. (see phenyl group and cage) Libration is usually determined by group inertia, attachment bonds, and the surroundings.
4. The more complex phenyl motion shown is due to whiplash caused by an internal warping motion in the cage.
5. The phenyl group has good rigid body (TLS) motion with pronounced screw (S) components, correlating libration (L), and translation (T).



Phenylhydroxynorbornanone
(50% Thermal Ellipsoids)

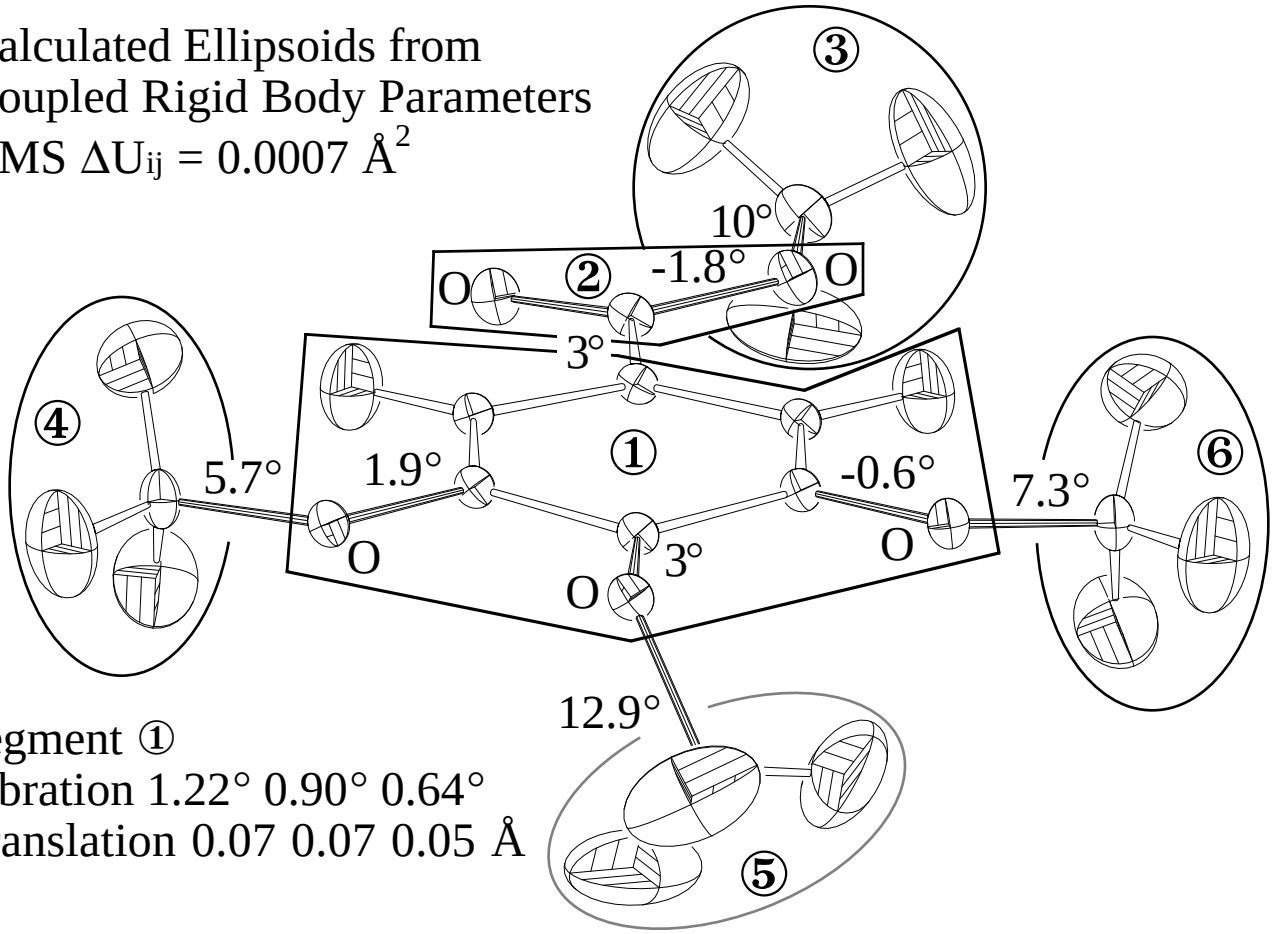
$Cr(CO)_3 \bullet (CH_3O)_3C_6H_2CO_2CH_3$

Allen Hunter
Youngstown State University



75% Thermal Ellipsoids
15 K Neutron Data
$R(F^2) = 5\%$

Calculated Ellipsoids from
Coupled Rigid Body Parameters
RMS $\Delta U_{ij} = 0.0007$ Å^2



Segment ①
Libration 1.22° 0.90° 0.64°
Translation 0.07 0.07 0.05 Å

Correlating Our Independent 3D Gaussians

Conceptual problems which arise when modeling atom thermal motion.

1. We talk about 3-n dimensional mean-square displacement spaces, but everything really happens over time in a common 3-dimensional space.

   Use infinite-dimensional **cylinder spaces** which project into finite dimensional probability subspaces integrated over time.

2. Each Gaussian function is infinite, but the thermal displacement of a well behaved atom is strictly local. Atoms do not often swap positions with other atoms.

   Use **separable spaces** that partition into one subspace per atom using topological or statistical methods.

3. Most atoms in crystals are very “territorial” and dislike being too crowded or too isolated.

   This would require mechanistic input assumptions such as atom-pair distance potential functions or molecular dynamics calculations.

To accommodate 1 and 2 into a probabilistic model, **Gaussian process** models using conditional distributions seem to be a promising new approach. We have some preliminary results along that line.

Radon-Nikodym Density

The characteristic equations (in an orthogonal reciprocal space coordinate system)

$$\phi_k(\mathbf{z}) = \exp\{i\mathbf{a}_k^t\mathbf{z} - {}^1/_2\mathbf{z}^t\mathbf{B}_k\mathbf{z}\} \quad k=1,2$$

define two adjacent atoms with means $\mathbf{a_1}, \mathbf{a_2}$ and temperature factor matrices $\mathbf{B_1}, \mathbf{B_2}$. The direct space Gaussian densities are:

$$\mu_k(\mathbf{x}) = (|\mathbf{B}_k^{-1}|/(2\pi)^{3/2}) \exp\{-(\mathbf{x}-\mathbf{a}_k)^t \mathbf{B}_k^{-1}(\mathbf{x}-\mathbf{a}_k)\} \quad k=1,2.$$

Using $\mathbf{B}_2^{-1/2}$ as a transformation matrix, we define

$$\mathbf{b} = \mathbf{B}_2^{-1/2}(\mathbf{a}_2-\mathbf{a}_1), \quad \mathbf{c}(\mathbf{x}) = \mathbf{B}_2^{-1/2}(\mathbf{x}-\mathbf{a}_1), \quad \mathbf{D_{2,1}} = \mathbf{B}_2^{-1/2}(\mathbf{B}_1-\mathbf{B}_2)\mathbf{B}_2^{-1/2},$$

where $\mathbf{D_{2,1}}$ is a **Hilbert-Schmidt matrix** (for atom 2 with respect to the reference atom 1) with 3 eigenvalues and eigenvectors denoted as λ_k and $\mathbf{e}_k$, k=1,2,3, respectively.

The **Radon-Nikodym density**, $\omega_{2,1}(\mathbf{x})$ defined as the derivative of $\mu_2(\mathbf{x})$ with respect to $\mu_1(\mathbf{x})$,

$$(d\mu_2/d\mu_1)(\mathbf{x}) = \exp\{-\tfrac{1}{2}[\sum_{k=1}^{3}(\mathbf{e}_k^t\mathbf{c}(\mathbf{x}))^2(\lambda_k/(1+\lambda_k)) - \ln(1+\lambda_k)] + \mathbf{c}^t(\mathbf{x})\,\mathbf{b} - 1/2\mathbf{b}^t\,\mathbf{b}\},$$

provides a mechanism for separation of the Gaussian atoms.

Ref: I.I. Gihman and A.V. Skorohod (1974), The Theory of Stochastic Processes I, Springer-Verlag, New York, NY, p. 496.

Properties of Radon-Nikodym Density

$$\omega_{2,1}(\mathbf{x}) = [d\mu_2 / d\mu_1](\mathbf{x})$$

1. Definition – $\omega_{2,1}(\mathbf{x})$ is an **absolutely continuous component** of Gaussian $\mu_2(\mathbf{x})$ with respect to Gaussian $\mu_1(\mathbf{x})$.

2. $\omega_{2,1}(\mathbf{x}) = 1$ defines a 4th order hyperplane surface separating $\mu_1(\mathbf{x})$ from $\mu_2(\mathbf{x})$ and bounds the **range** of $\mu_1(\mathbf{x})$.

   (a) At this surface we have the equalities:
   $\mu_2(\mathbf{x}) = \mu_1(\mathbf{x})$, (i.e., densities are equal), and
   $\omega_{2,1}(\mathbf{x}) = [1/\omega_{2,1}(\mathbf{x})] = [d\mu_1 / d\mu_2](\mathbf{x}) = \omega_{1,2}(\mathbf{x})$

   (b) The partition is planar if it lies in a mirror of symmetry or pseudo-symmetry for the atom pair, but **nonplanar partition surfaces** are the general rule.

3. At the μ_1 mean (a_1), $\omega_{2,1}(\mathbf{x})$ is a minimum and increases along $\omega_{2,1}(\mathbf{x})$ **fibers** which terminate at the partition $\omega_{2,1}(\mathbf{x}) = 1$.

4. The **chain rule** of differentiation applies, i.e.,
   $(dp / dq) = (dp / dr)\,(dr / dq)$; thus,
   (a) The boundaries for three adjacent atoms meet in a line (in general a **curved polyhedral edge**).
   (b) The boundaries for four (highly) non-coplanar adjacent atoms meet at a point (a **polyhedral vertex**).

5. Partitions arising from all first neighbors around any $\mu(\mathbf{x})$ define a **"dented ball" range and boundary** for that $\mu(\mathbf{x})$.

6. The $\omega_{i,j}(\mathbf{x}) = 1$ **statistical partitioning** is *not* critical-point topology partitioning; but, the vertices, edge midpoints, face centroids, and μ mean sites of the former will be close to the **pit, pale, pass,** and **peak critical points** of the latter.

Properties of the Hilbert-Schmidt Matrix

Hilbert-Schmidt ($\mathbf{D} = \mathbf{B}_2^{-1/2} (\mathbf{B}_1 - \mathbf{B}_2) \mathbf{B}_2^{-1/2}$) Calculations.
Eigenvector 1 of **D** is always near the Interatomic Vector.

	Partition Point	Eigenvalues D(1)	D(2)	D(3)
From Normal Coord. Anal.				
2 C-H (RT)	0.34(1)	-0.74(1)	-0.94	-0.95
From 6 Neutron Structures				
14 C-H (15K)	0.41(3)	-0.52(9)	-0.73(4)	-0.79(5)
13 C-H (RT)	0.51(1)	-0.06(6)	-0.35(3)	-0.51(5)
15 C-H (RT)	0.51(2)	-0.05(13)	-0.39(5)	-0.52(3)
5 C-H (RT)	0.50(2)	-0.13(5)	-0.43(8)	-0.55(5)
14 C-H (RT)	0.52(2)	0.02(12)	-0.42(5)	-0.58(6)
8 N-H (RT)	0.50(1)	-0.06(5)	-0.31(11)	-0.43(5)

The above include two phenyl norbornanol derivatives, a TCNQ-benzene adduct, a photodimer with 3 methyl groups, a tetrathiourea derivative, and a methylether complex synthesized by Allen Hunter. The normal coordinate results are for cyclobutane.

- “Partition Point” is where the partition plane intersects the C-H bond.
- The coefficients of the matrix **D** are dimensionless.
- When used for terminal C-H, **D** is roughly identical numerically for all groups containing C-H bonds, even methyl groups.
- **D** is temperature sensitive because of H zero-point energy. Note the much larger coefficients at 15 K.
- N-H groups seem to behave differently than C-H groups.
- O-H groups definitely behave differently because of H-bonding, but a C=O seems to have thermal motion which mimics that of C-H at room temperature.

Future Research Possibilities

A. Methods by **Hans-Beat Bürgi, his coworkers, and others** combining rigid bodies, spectroscopic normal coordinate analyses, and quantum mechanics calculations provide a valid and fruitful approach. (Ref: M. Fortsch (1997), Normal Mode Analysis from Atomic Mean Square Displacement Amplitudes, Ph.D. Thesis, Bern University.)

B. Probabilistic approaches using modern **Gaussian measure theory** have yet to be applied by crystallographers but seem to offer a promising approach, for example:

1. **Vector-valued Gaussian Measures** with the atoms of the asymmetric unit as Hilbert-Schmidt forms in an Ito-Weiner stochastic model. (Ref: A.A. Doregovtsev (1994), Stochastic Analysis and Random Maps in Hilbert Space, VSP, Utrecht)

2. **Conditional probability thermal-motion** program for automatic growth of coupled rigid-body models using a graph-based iterative likelihood function. (Ref: S.L. Lauritzen (1996), Graphical Models, Clarendon Press, Oxford.)

3. Better estimates of interatomic **distance corrections** for atom-pair thermal motion using first and second order Gaussian Chaos. (Ref: M. Ledoux and M. Talagrand (1991), Probability in Banach Spaces: Isoperimetry and Processes, Springer, p. 65, p. 326.)

Mathematical Literature References

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E. Vanmarcke (1983), Random Fields: Analysis and Synthesis, MIT Press, Cambridge, MA. ****

****	Prerequisite Reading	**	Gaussian Measures (short)
***	Gaussian Measures (long)	*	Specialized Topics