LECTURE #1: FOURTH AGE OF QUANTUM CHEMISTRY: MOLECULES IN MOTION

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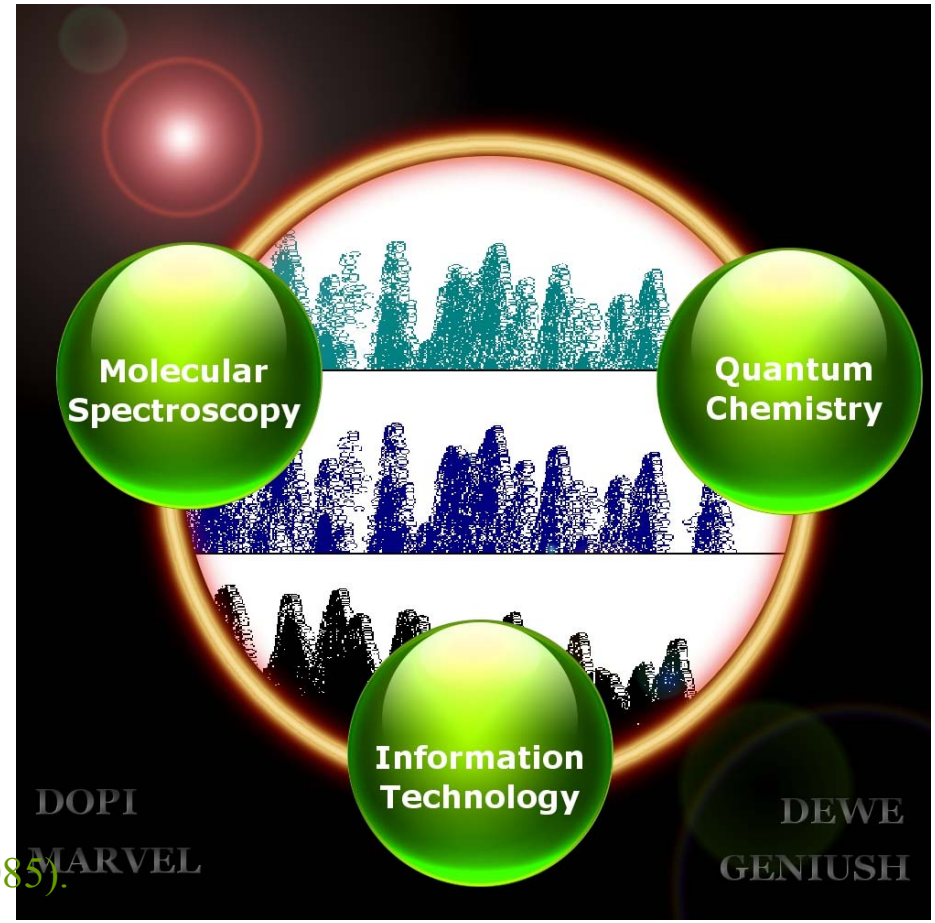
Winter School in Theoretical Chemistry
Helsinki, Finland, December 17-20, 2012

OUTLINE

- Introduction
- First-principles nuclear motion techniques
- RRHO (GF, SQM)
- VPT2 (1-D AHO)
- Variational techniques
- Outlook



Front cover of *Phys. Chem. Chem. Phys.* (A. G. Császár, C. Fábri, T. Szidarovszky, T. Furtenbacher, E. Mátyus, G. Czakó: Fourth age of quantum chemistry - molecules in motion, **2011,** *14*, 1085).

Pure Appl. Chem., Vol. 72, No. 8, pp. 1405–1423, 2000.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

QUANTUM CHEMISTRY IN THE 21st CENTURY

(Special Topic Article)

Prepared for publication by
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Abstract: Quantum chemistry is the field in which solutions to the Schrödinger equation are used to predict the properties of molecules and solve chemical problems. This paper considers possible future research directions in light of the discipline's past successes. After decades of incremental development—accompanied by a healthy dose of skepticism from the experimental community—the ready availability of fast computers has ushered in a "golden age" of quantum chemistry. In this new era of acceptance, theoretical predictions often precede experiment in small molecule chemistry, and quantum chemical methods play an ever greater role in biochemical and other larger systems. Quantum chemists increasingly divide their efforts along three fronts: high-level (spectroscopic) accuracy for small molecules, characterized by such techniques as Brueckner methods, r_{12} formalisms, and multireference calculations; parameterization- or extrapolation-based intermediate-level schemes (such as Gaussian-N theory) for medium molecules; and lower-level (chemical) accuracy for large molecules, characterized by density functional theory and linear scaling techniques. These tools, and quantum chemistry as a whole, are examined here from a historical perspective and with a view toward their future applications.

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"Third age of quantum chemistry"

$H\Psi = (T + V)\Psi = E\Psi$

	Electronic structure	Nuclear motion
Coordinates	Cartesian	Different internals
Kinetic energy	Simple form	Complex form
Potential energy	Known exactly	Unknown (PES)
Basis set	Consensus (GTO)	No consensus
Representation	FBR	VBR, FBR, DVR
# of Eigenvalues	One or a few	(Very) many
Diagonalization	Direct + iterative	Direct + iterative
Approximations	PT + VAR	PT + VAR

Similarities between electronic structure and certain nuclear motion techniques

Electronic structure	Nuclear motion
Hartree-Fock	Vibrational SCF
MP2	VMP
MC-SCF	VMC-SCF
CI	VCI
Full-CI with CBS	Variational FBR

(Lecturers:
Joel Bowman, Ove Christiansen)

Computational quantum chemistry

- Born-Oppenheimer approximation: separation of **nuclear** and electronic motions
- **PESs** for nuclear motions provided by electronic structure computations
- two Schrödinger-equations: **time-independent** and time-dependent view
- time-dependent picture: classical dynamics and quantum **dynamics**
- accurate **variational** approaches

Solution strategies to the electronic structure problem (PES, DMS)

Traditional *ab initio* (wavefunction-based) routes

- Perturbational
  - MP*n* series
- Variational
  - (IC)(MR)CI*n* series
- Coupled cluster
  - (MR)CC*n* series

Accuracy goals in electronic structure computations

	atomic units	kJ mol^{-1}	cm^{-1}
Chemical accuracy	$\approx$1 mE_h	4	
Calibration accuracy	$\approx$0.2 mE_h	1	$\approx$100
Spectroscopic accuracy	$\approx$1 μE_h		1
Hyperfine accuracy	$\approx$1 nE_h		

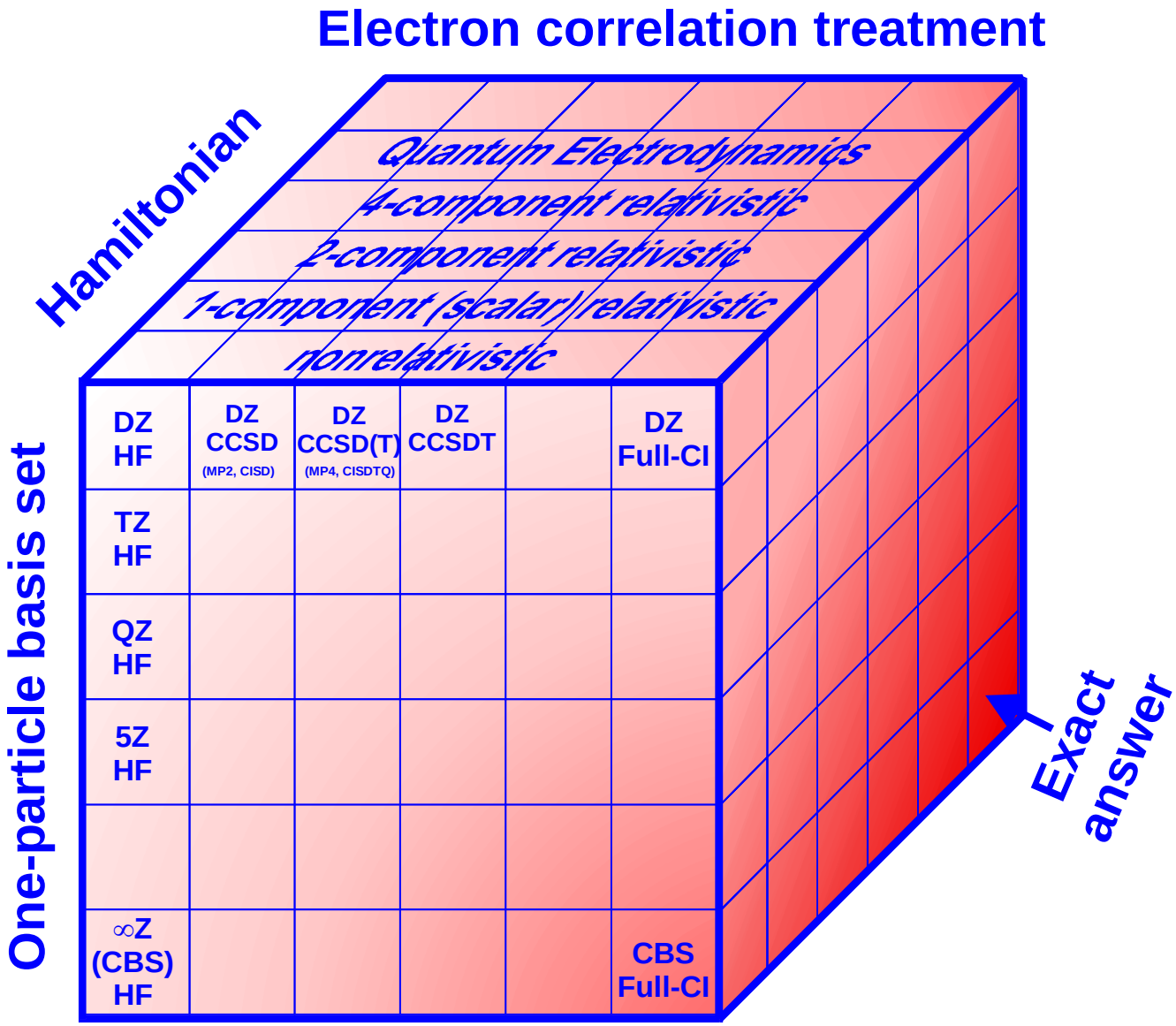
NB1: Obviously, it is much harder to achieve these accuracy goals in absolute energies than in relative energies chemists are mostly interested in.
NB2: These accuracies are characteristic of theoretical treatments, they have nothing to do with accuracies related to spectroscopic measurements.

Motivations of the composite focal-point analysis (FPA) approach

- Get the right result for the right reason for polyatomic and polyelectronic systems.
- Attach error bars to theoretical predictions.
- Consider small physical effects tacitly neglected in most quantum chemical studies, such as core correlation, relativistic effects, and corrections to the Born-Oppenheimer approximation.
- Approach spectroscopic accuracy (1 cm^{-1}) as opposed to chemical (1 kcal mol^{-1}) or calibration (1 kJ mol^{-1}) accuracy in predictions of spectra.

W. D. Allen, A. L. L. East, A. G. Császár, *Structures and Conformations of Non-Rigid Molecules*, edited by J. Laane, M. Dakkouri, B. van der Veken and H. Oberhammer (Kluwer, Dordrecht, **1993**), pp. 343-373.

A. G. Császár, W. D. Allen, H. F. Schaefer III, *J. Chem. Phys.* **1998**, *108*, 9751.



G. Tarczay, A. G. Császár, W. Klopper, H. M. Quiney, *Mol. Phys.* **2001**, *99*, 1769-1794

Incremental (FPA) buildup of the adiabatic (CVRQD) PESs of water

Valence-only problem

nearly complete basis set (extrapolated) IC-MRCI

Core-correlation correction (at present ACPF or all-electron)

Relativistic corrections

one-electron mass-velocity and Darwin (MVD1)
two-electron Darwin (D2)
Gaunt and Breit corrections
quantum electrodynamics (QED)

Adiabatic and nonadiabatic Born-Oppenheimer corrections

A. G. Császár, W. D. Allen, and H. F. Schaefer, *J.Chem. Phys.* **108**, 9751 (1998).
O. L. Polyansky, A. G. Császár, J. Tennyson, P. Barletta, S. V. Shirin, N. F. Zobov, D. W. Schwenke, and P. J. Knowles, *Science* **299,** 539 (2003).

Corrections, in cm^{-1}, to the vibrational states of H_2O and H_2S

Correction surface	$H_2{}^{16}O$		$H_2{}^{32}S$	
	stretch	bend	stretch	bend
MVD1	$-2.8(n_1+n_3)$	$+1.4n_2$	$-4.2(n_1+n_3)$	$+0.7n_2$
D2	$-0.04(n_1+n_3)$	$+0.12n_2$	$-0.05(n_1+n_3)$	$+0.38n_2$
Gaunt	$-0.8(n_1+n_3)$	n.a.	$-0.52(n_1+n_3)$	$-0.12n_2$
Retard.	$+0.15(n_1+n_3)$	$-0.02n_2$	$+0.12(n_1+n_3)$	$+0.02n_2$
Lamb-shift	$+0.18(n_1+n_3)$	$-0.11n_2$	$-0.40(n_1+n_3)$	$+0.00n_2$
Core el.	$+7.3(n_1+n_3)$	$-0.5n_2{}^2$	$+5.1(n_1+n_3)$	$+2.0n_2$
DBOC	$+0.4(n_1+n_3)$	$-0.45n_2$	$+0.4(n_1+n_3)$	$+0.6-0.2n_2$

O. L. Polyansky, A. G. Császár *et al.*, *Science* **299**, 539 (2003).

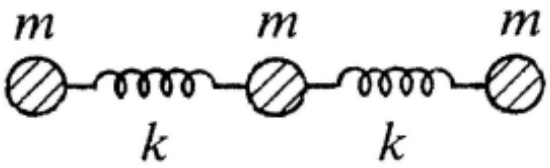
Treating quantum motions of nuclei

- **Qualitative understanding of nuclear motion**
  RRHO (rigid rotor – harmonic oscillator)
  - SQM force fields, GF method, simple model problems

- **Interpretation of experimental results**
  Perturbative approaches, anharmonic force fields
  - Local vs normal modes, VPT2, higher-order PT

- **Fourth age: moving (much) beyond fixed nuclei**
  Variational approaches
  - VBR
  Grid-based (nearly variational) approaches
  - FBR ↔ DVR

The simple RRHO model



- harmonic oscillators – normal modes
- Eckart embedding
- rigid rotors
- exact and approximate quantum numbers
- reference book: E. B. Wilson, J. C. Decius, P. C. Cross: *Molecular Vibrations*, Dover, New York, 1980

The GF method

Descartes displacement coordinates

$$x_\alpha = a_\alpha - a_{\alpha,0},\ y_\alpha = b_\alpha - b_{\alpha,0},\ z_\alpha = c_\alpha - c_{\alpha,0}$$

$$T = \tfrac{1}{2}\sum_{\alpha=1}^{N} m_\alpha \left[\left(\frac{d\,x_\alpha}{dt}\right)^2 + \left(\frac{d\,y_\alpha}{dt}\right)^2 + \left(\frac{d\,z_\alpha}{dt}\right)^2 \right]$$

Descartes mass-weighted displacement coordinates

$$\begin{array}{lll} q_1 := \sqrt{m_1}\,x_1 & q_4 := \sqrt{m_2}\,x_2 & \ldots \quad q_{3N-2} := \sqrt{m_N}\,x_N \\ q_2 := \sqrt{m_1}\,y_1 & q_5 := \ldots & q_{3N-1} := \sqrt{m_N}\,y_N \\ q_3 := \sqrt{m_1}\,z_1 & & q_{3N} := \sqrt{m_N}\,z_N \end{array}$$

$$T = \tfrac{1}{2}\sum_{i=1}^{3N}\left(\frac{d\,q_i}{dt}\right)^2 = \tfrac{1}{2}\sum_{i=1}^{3N}\dot{q}_i^2 = \tfrac{1}{2}\begin{pmatrix}\dot{q}_1 & \dot{q}_2 & \ldots & \dot{q}_{3N}\end{pmatrix}\begin{pmatrix}\dot{q}_1 \\ \dot{q}_2 \\ \vdots \\ \dot{q}_{3N}\end{pmatrix} = \tfrac{1}{2}\dot{\mathbf{q}}^T\dot{\mathbf{q}}$$

The GF method

Representation of potential energy surface (PES)

$$V(\mathbf{x}) = V_0 + \tfrac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} H_{ij} x_i x_j = V_0 + \tfrac{1}{2}\mathbf{x}^T \mathbf{H}\mathbf{x}$$

$$V(\mathbf{q}) = V_0 + \tfrac{1}{2}\mathbf{q}^T \mathbf{W}\mathbf{q}$$

Lagrange formalism

$$L(\mathbf{q}, \dot{\mathbf{q}}; t) = T - V \qquad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$$

$$\boxed{\ddot{\mathbf{q}} + \mathbf{W}\mathbf{q} = \mathbf{0}}$$

Introduction of normal coordinates

$$Q_k = \sum_{i=1}^{3N} U_{ik} q_i \quad \ddot{\mathbf{Q}} + \mathbf{\Lambda}\mathbf{Q} = \mathbf{0} \;\Rightarrow\; \left(\frac{d^2 Q_k}{dt^2}\right) + \lambda_k Q_k = 0 \;,\; k = 1, 2, \ldots, 3N$$

The GF method

1. $T = \frac{1}{2} m v^2 \Rightarrow 2T = \sum_{i=1}^{3N} \dot{\rho}_i^2 = \dot{\boldsymbol{\rho}}^T \dot{\boldsymbol{\rho}}$

2. $V = \frac{1}{2} k x^2 \Rightarrow 2V = \sum_{ij} F_{ij} \rho_i \rho_j$

3. $d_{i\alpha} = r_{i\alpha} - a_{i\alpha}$

4. $2T = \left(\dot{\mathbf{d}}^T \mathbf{M}^{1/2}\right)\left(\mathbf{M}^{1/2} \dot{\mathbf{d}}\right)$

5. $\mathbf{s} = \mathbf{B}\mathbf{d}$

6. $2T = \dot{\mathbf{s}}^T (\mathbf{B}^{-1})^T \mathbf{M} \mathbf{B}^{-1} \dot{\mathbf{s}}$

7. $\mathbf{G} = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^T$

8. $\mathbf{s} = \mathbf{L}\mathbf{Q}$

$$2T = \dot{\mathbf{s}}^T \mathbf{G}^{-1} \dot{\mathbf{s}} \qquad\qquad 2V = \mathbf{s}^T \mathbf{F} \mathbf{s}$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$2T = (\dot{\mathbf{Q}}^T \mathbf{L}^T)\mathbf{G}^{-1}(\mathbf{L}\dot{\mathbf{Q}}) \qquad\qquad 2V = (\mathbf{Q}^T \mathbf{L}^T)\mathbf{F}(\mathbf{L}\mathbf{Q})$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\mathbf{L}^T \mathbf{G}^{-1} \mathbf{L} = \mathbf{I} \qquad\qquad \mathbf{L}^T \mathbf{F} \mathbf{L} = \boldsymbol{\Lambda}$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\mathbf{L}\mathbf{L}^T = \mathbf{G} \qquad \Rightarrow \qquad \boxed{(\mathbf{G}\mathbf{F})\mathbf{L} = \mathbf{L}\boldsymbol{\Lambda}}$$

The GF method in Cartesian space

translation

$$T_1 = N_1 \sum_{\alpha=1}^{N} m_\alpha^{1/2} q_{x\alpha}$$

$$T_2 = N_2 \sum_{\alpha=1}^{N} m_\alpha^{1/2} q_{y\alpha}$$

$$T_3 = N_3 \sum_{\alpha=1}^{N} m_\alpha^{1/2} q_{z\alpha}$$

rotation

$$R_1 = N_1 \sum_{\alpha=1}^{N} m_\alpha^{1/2} \left(b_\alpha q_{z\alpha} - c_\alpha q_{y\alpha} \right),$$

$$R_2 = N_2 \sum_{\alpha=1}^{N} m_\alpha^{1/2} \left(c_\alpha q_{x\alpha} - a_\alpha q_{z\alpha} \right)$$

$$R_3 = N_3 \sum_{\alpha=1}^{N} m_\alpha^{1/2} \left(a_\alpha q_{y\alpha} - b_\alpha q_{x\alpha} \right)$$

$q_{x\alpha} = \sqrt{m_\alpha}\,\Delta x_\alpha$ α for atoms

a_α, b_α, c_α equilibrium (reference) coordinates

$$\boxed{(\mathbf{M}^{-1}\mathbf{F}^{X})\mathbf{L}^{X} = \mathbf{L}^{X}\mathbf{\Lambda}}$$

Total energy distribution (TED)

Classical mechanical expressions:

$$T = \frac{1}{2}\sum_{ij} G_{ij}^{-1}\dot{S}_i\dot{S}_j \qquad V = \frac{1}{2}\sum_{ij} F_{ij} S_i S_j$$

Molecule moves only along normal coordinate *k*:

$$S_i = L_{ik}Q_k \qquad \dot{S}_i = L_{ik}\dot{Q}_k$$

$$T_k = \frac{\dot{Q}_k^2}{2}\left(\sum_{ij} G_{ij}^{-1}L_{ik}L_{jk}\right) = \frac{\dot{Q}_k^2}{2}\left(\sum_i [\mathrm{KED}]_i^k\right)$$

$$V_k = \frac{Q_k^2}{2}\left(\sum_{ij} F_{ij} L_{ik}L_{jk}\right) = \frac{\lambda_k Q_k^2}{2}\left(\sum_i [\mathrm{PED}]_i^k\right)$$

$$[\mathrm{KED}]_i^k = \sum_j (L_{ik}G_{ij}^{-1}L_{jk}) \qquad \boxed{[\mathrm{PED}]_i^k = \sum_j (L_{ik}F_{ij}L_{jk})/\lambda_k}$$

$$\mathbf{C} = \mathbf{G}^{-1/2}\mathbf{L} \qquad \mathbf{G}^{-1}\mathbf{L} = \left(\mathbf{L}^{-1}\right)^T \qquad \mathbf{G} = \mathbf{L}\mathbf{L}^T$$

$$[\mathrm{KED}]_i^k = [\mathrm{PED}]_i^k = L_{ik}L_{ki}^{-1} \qquad \boxed{[\mathrm{TED}]_i^k = L_{ik}L_{ki}^{-1}}$$

TED best describes contribution of internal coordinates to a normal coordinate

Normal Mode Decomposition (NMD)

$$NMD_{iJ}^2 = \left\langle \psi_i \middle| Q_J^{HO} \right\rangle^2$$

HNCO

,,Fundamentals"

	4681.3 Q_0	572.4 Q_5	637.0 Q_6	818.1 Q_4	1144.8 Q_{5+5}	1209.4 Q_{5+6}	1274.0 Q_{6+6}	1318.3 Q_3	1390.5 Q_{4+5}	1455.1 Q_{4+6}	1636.2 Q_{4+4}	1717.2 Q_{5+5+5}	1781.8 Q_{5+5+6}		Sum
4631.0	98	0	0	0	0	0	0	0	0	0	0	0	0	…	99
579.5	0	95	0	1	0	0	0	0	0	0	0	0	0	…	97
660.2	0	0	99	0	0	0	0	0	0	0	0	0	0	…	99
780.7	0	2	0	90	0	0	0	0	0	0	2	0	0	…	96
1146.8	0	0	0	0	80	0	6	5	0	0	0	0	0	…	93
1267.1	0	0	0	0	3	0	26	41	20	0	0	0	0	…	94
1275.1	0	0	0	0	0	91	0	0	0	5	0	0	0	…	97
1329.3	0	0	0	2	4	0	11	45	22	0	4	0	0	…	92
1358.6	0	0	0	2	7	0	54	5	15	0	7	0	0	…	93
1476.6	0	0	0	0	0	7	0	0	0	88	0	0	0	…	97
1521.6	0	0	0	2	0	0	2	0	28	0	51	0	0	…	91
1712.7	0	0	0	0	0	0	0	0	0	0	0	69	0	…	90
1843.6	0	0	0	0	0	0	0	0	0	0	0	0	45	…	96
	…	…	…	…	…	…	…	…	…	…	…	…	…		
Sum	98	99	98	95	98	99	99	94	98	95	92	95	98		

E. Mátyus, C. Fábri, T. Szidarovszky, G. Czakó, W. D. Allen, and A. G. Császár, *J. Chem. Phys.* **2010**, *133*, 034113.

Rigid-rotor decomposition (RRD) tables for ketene (H_2CCO)

A_1	RRD$(\nu_{rv}, \nu_v)^{a,b}$	ν_v	603.5(B_1)	603.5(B_1)	437.1(B_2)	437.1(B_2)	534.0(B_1)
	ν_{rv}	$J_{K_aK_c}$	3_{13}	3_{31}	3_{12}	3_{30}	3_{31}
	617.5		99	0	1	0	0
	697.4		0	94	0	5	1

A_2	RRD$(\nu_{rv}, \nu_v)^{a,b}$	ν_v	603.5(B_1)	603.5(B_1)	437.1(B_2)	437.1(B_2)	534.0(B_1)
	ν_{rv}	$J_{K_aK_c}$	3_{12}	3_{30}	3_{13}	3_{31}	3_{30}
	617.5		99	0	1	0	0
	697.4		0	94	0	5	1

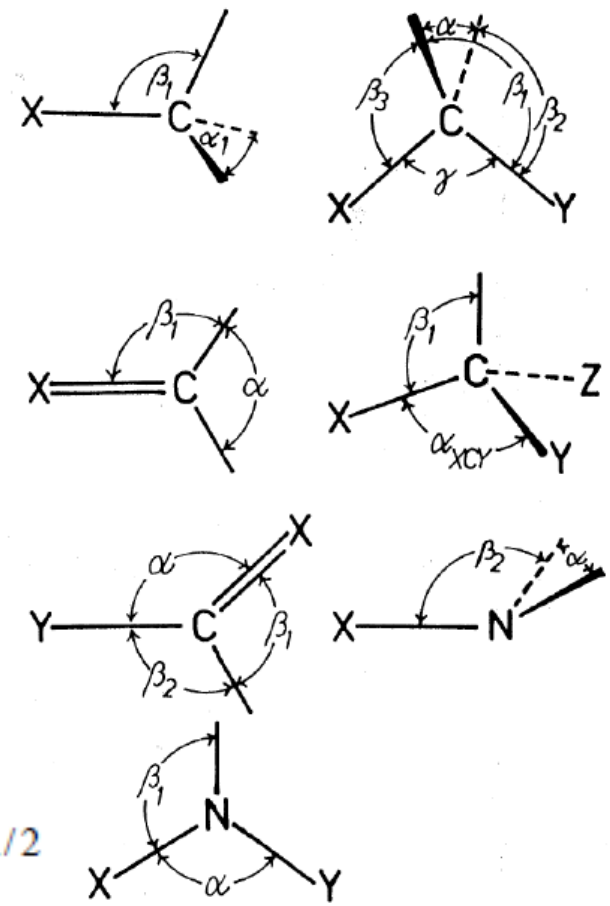
B_1	RRD$(\nu_{rv}, \nu_v)^{a,b}$	ν_v	603.5(B_1)	437.1(B_2)
	ν_{rv}	$J_{K_aK_c}$	3_{22}	3_{21}
	647.4		98	2

B_2	RRD$(\nu_{rv}, \nu_v)^{a,b}$	ν_v	603.5(B_1)	603.5(B_1)	437.1(B_2)
	ν_{rv}	$J_{K_aK_c}$	3_{03}	3_{21}	3_{22}
	607.5		100	0	0
	647.4		0	98	2

C. Fábri, E. Mátyus, T. Furtenbacher, B. Mihály, T. Zoltáni, L. Nemes, and A. G. Császár, *J. Chem. Phys.* **2011**, *135*, 094307.

The scaled quantum mechanical (SQM) force field technique

- level: HF/4-21G or B3LYP/6-31G*
- choice of natural internal coordinates
- shifted reference geometry
- computation of quadratic force constants (analytic vs. numerical)
- computation of displaced structures
- scaling of quadratic force fields



$$\mathbf{x}^1 = \mathbf{x}_0 + \mathbf{A}\mathbf{q} \quad \mathbf{A} = \mathbf{m}\mathbf{B}^T(\mathbf{B}\mathbf{m}\mathbf{B}^T)^{-1} \quad \mathbf{F} = \mathbf{C}^{1/2}\mathbf{F}^{\mathrm{elm}}\mathbf{C}^{1/2}$$

P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, A. Vargha, *J. Am. Chem. Soc.* **105**, 7037 (1983).
W. D. Allen, A. G. Császár, D. A. Horner, *J. Am. Chem. Soc.* **114**, 6834 (1992).

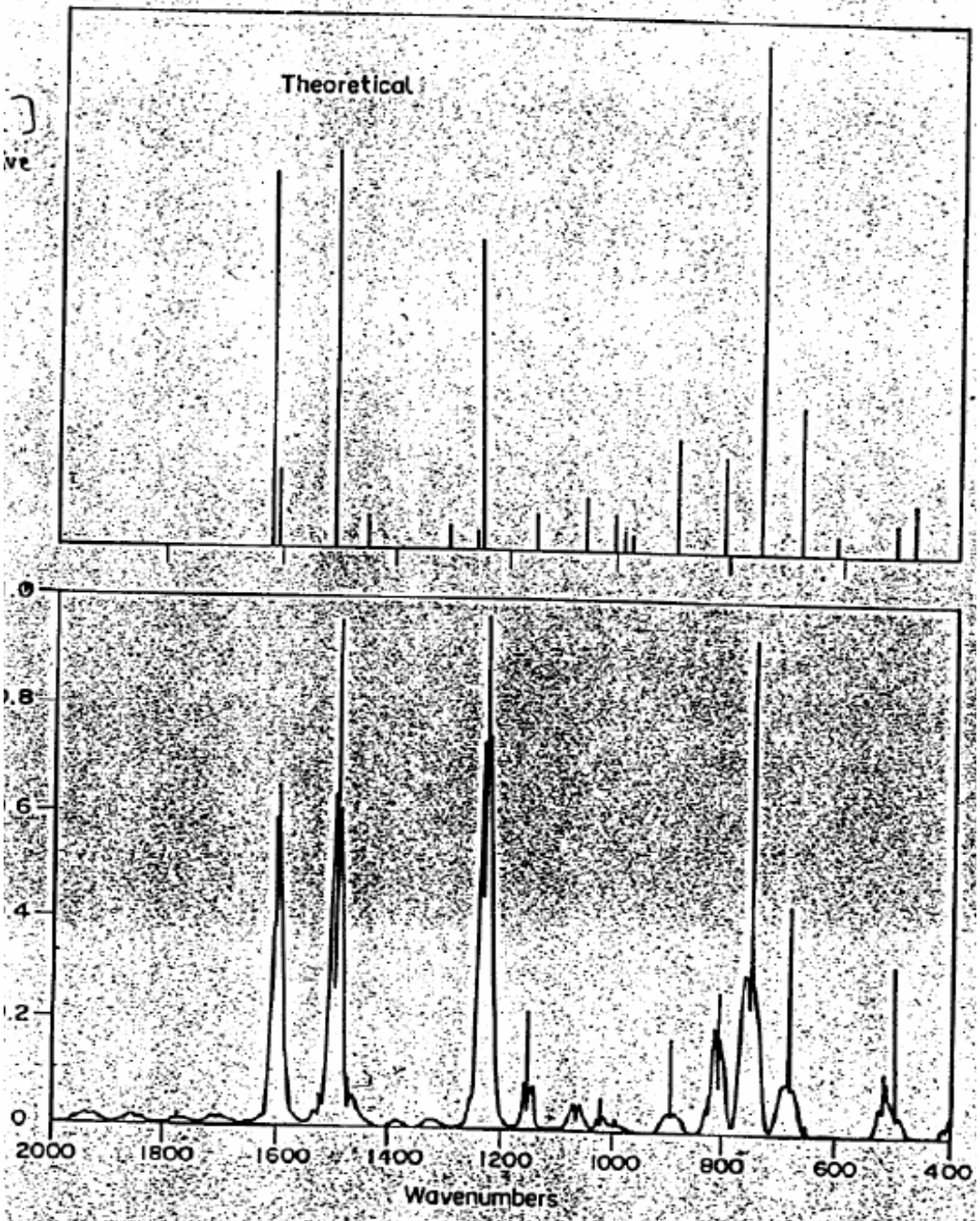


Fig. 2. Experimental and theoretical i.r. spectrum of fluorobenzene.

Second-order vibrational perturbation theory (VPT2)

- complex derivations, complex formulas but overly inexpensive way to obtain accurate spectroscopic constants
- applicable for large (semirigid) molecules
- there are higher-order PT schemes, as well
- VPT2 almost exact for stretching motion (see below)

Anharmonic 1-D oscillator

$$\hat{H} = \hat{H}^0 + \hat{H}' = \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) + bx^4$$

treating **quartic** term with PT1

$$E_n^0 = \left(n + \tfrac{1}{2}\right)h\nu \ ,$$

zeroth-order solutions

$$u_n^0(x) = \left(\frac{1}{2^n n!}\sqrt{\frac{\alpha}{\pi}} \right)^{1/2} \exp(-\alpha x^2/2) H_n(\sqrt{\alpha}x)$$

$$E_n^{(1)} = \langle n | bx^4 | n \rangle = \int_{-\infty}^{+\infty} u_n^0(x)^* \left[bx^4 \right] u_n^0(x) dx$$

$$\left(x^4\right)_{nn} = \sum_k \left(x^2\right)_{nk}\left(x^2\right)_{kn}$$

$$x_{n,k} \equiv \langle n | x | k \rangle = \delta_{k,n+1}\sqrt{\frac{n+1}{2\alpha}} + \delta_{k,n-1}\sqrt{\frac{n}{2\alpha}}$$

$$\left(x^2\right)_{n,n+2} = \sum_k (x)_{n,k}(x)_{k,n+2} = x_{n,n+1}x_{n+1,n+2} = \sqrt{\frac{n+1}{2\alpha}}\sqrt{\frac{n+2}{2\alpha}} = \frac{\sqrt{(n+1)(n+2)}}{2\alpha}$$

$$\left(x^2\right)_{n,n} = x_{n,n+1}x_{n+1,n} + x_{n,n-1}x_{n-1,n} = \frac{n+1}{2\alpha} + \frac{n}{2\alpha} = \frac{(2n+1)}{2\alpha} \ ,$$

$$\left(x^2\right)_{n,n-2} = \sum_k (x)_{n,k}(x)_{k,n-2} = x_{n,n-1}x_{n-1,n-2} = \frac{\sqrt{n(n-1)}}{2\alpha} \ .$$

Anharmonic 1-D oscillator

$$\left(x^4\right)_{nn} = \frac{1}{4\alpha^2}\left[(n+1)(n+2)+n(n-1)+4n^2+4n+1\right] = \frac{3}{2\alpha^2}(n^2+n+\tfrac{1}{2})$$

$$\boxed{E_n^{(1)} = \frac{3b}{2\alpha^2}\left[(n+\tfrac{1}{2})^2+\tfrac{1}{2}\right]}$$

$$u_0 = u_0^0 + \frac{\langle 1|\hat{H}'|0\rangle}{E_0^0 - E_1^0}u_1^0 + \frac{\langle 2|\hat{H}'|0\rangle}{E_0^0 - E_2^0}u_2^0 + \frac{\langle 3|\hat{H}'|0\rangle}{E_0^0 - E_3^0}u_3^0 + \ldots$$

second and fourth (etc.) expressions on r.h.s. are exactly zero

$$\left(x^4\right)_{n,n-2} = x_{n,n}^2 x_{n,n-2}^2 + x_{n,n-2}^2 x_{n-2,n-2}^2 = \frac{2n+1}{2\alpha}\frac{\sqrt{n(n-1)}}{2\alpha} + \frac{\sqrt{n(n-1)}}{2\alpha}\frac{2n-3}{2\alpha} =$$

$$= \frac{(2n-1)\sqrt{n(n-1)}}{2\alpha^2}$$

$$\boxed{u_0 = u_0^0 - \frac{3\sqrt{2}b}{4\alpha^2 h\nu}u_2^0 + \ldots}$$

Anharmonic 1-D oscillator

$$\hat{H} = \hat{H}^0 + \hat{H}' = \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) + ax^3$$

treating **cubic** term with PT2 ($E_n^{(1)} = \langle n | ax^3 | n \rangle = 0$)

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \langle n | \hat{H}' | k \rangle \right|^2}{E_n^0 - E_k^0}$$

$$\langle n | ax^3 | m \rangle = a \sum_k \langle n | x^2 | k \rangle \langle k | x | m \rangle$$

k only n or $n \pm 2$ m only $n \pm 3$ or $n \pm 1$

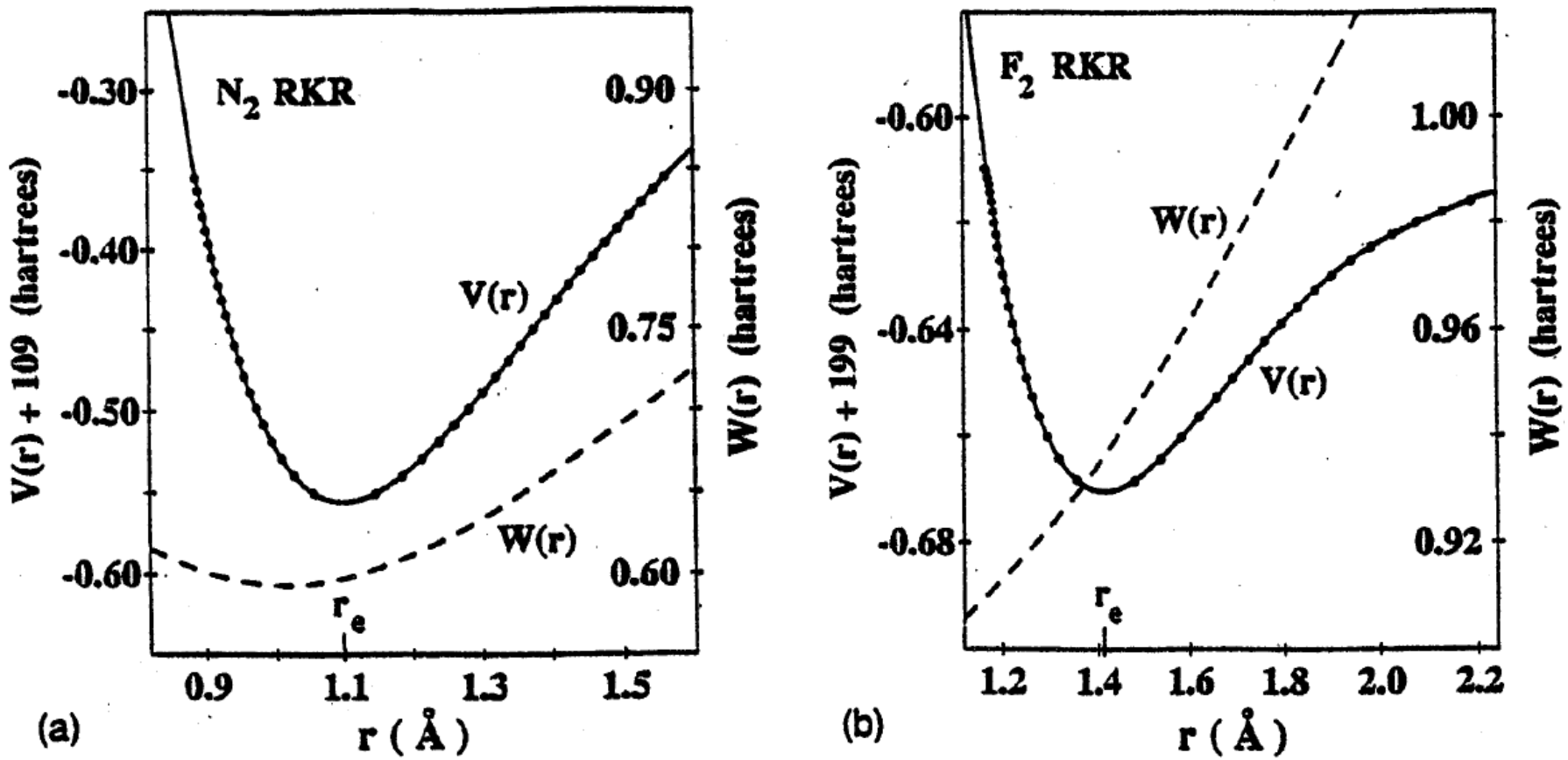
$$E_n^{(2)} = \frac{\left| \langle n | ax^3 | n+3 \rangle \right|^2}{E_n^0 - E_{n+3}^0} + \frac{\left| \langle n | ax^3 | n+1 \rangle \right|^2}{E_n^0 - E_{n+1}^0} + \frac{\left| \langle n | ax^3 | n-1 \rangle \right|^2}{E_n^0 - E_{n-1}^0} + \frac{\left| \langle n | ax^3 | n-3 \rangle \right|^2}{E_n^0 - E_{n-3}^0}$$

$$a(x^3)_{n,n+3} = a(x^2)_{n,n+2}(x)_{n+2,n+3} = a\sqrt{\frac{(n+1)(n+2)(n+3)}{(2\alpha)^3}}$$

etc.

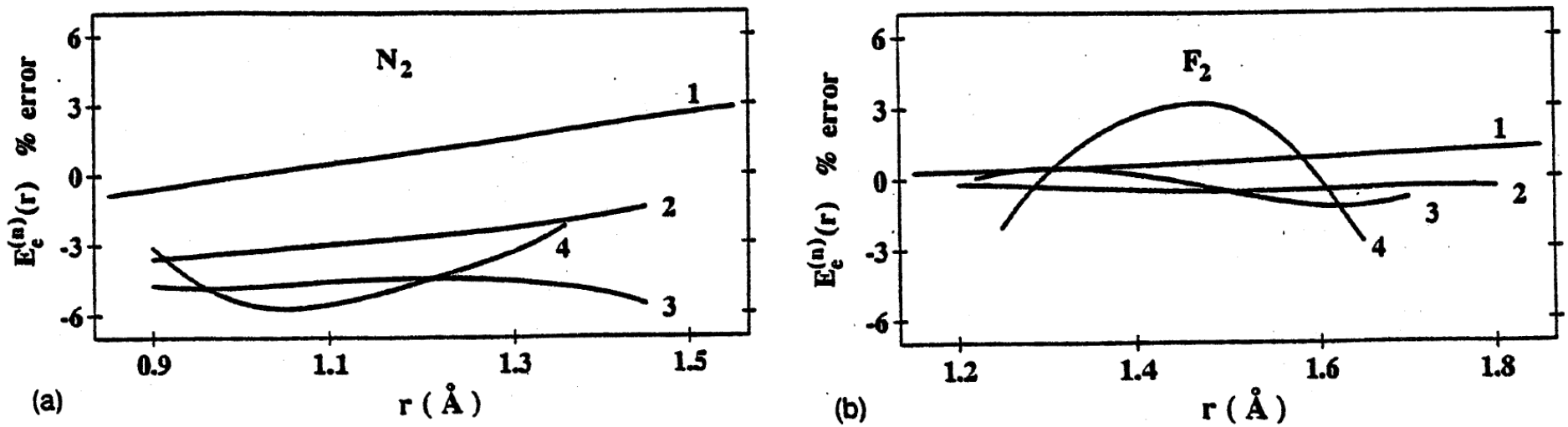
$$\boxed{E_n^{(2)} = -\frac{30a^2}{h\nu(2\alpha)^3}\left[\left(n + \tfrac{1}{2}\right)^2 + \frac{7}{60} \right]}$$

Quartic force field representation of PESs



$$W(r) \equiv V_{\mathrm{RHF}}(r) - V_{\mathrm{RKR}}(r)$$

Quartic force field representation of PESs



Percent error curves of electronic energy derivative curves

Quartic force field representation of PESs

TABLE III. A comparison of DZP RHF theoretical and RKR experimental data for the electronic (E_e) and total (V) energies of F_2 and their geometric derivatives through fourth order.[a]

	At r_e(DZP RHF) = 1.334 980 Å			At r_e(expt) = 1.411 930 Å			
	DZP RHF	RKR	% error	DZP RHF	RKR	% error	PZ(3d2f1g) CCSD(T)
$E_e(F_2)$	−230.847 255	−231.773 494	−0.40	−229.092 257	−230.027 524	−0.41	−229.724 951
E_e'	104.859	104.371	0.47	94.277	93.741	0.57	93.735
E_e''	−148.28	−148.98	−0.5	−127.42	−128.08	−0.5	−128.00
E_e'''	298.1	296.8	0.4	245.9	245.7	0.08	247.1
E_e''''	−755.4	−745.8	1.3	−604.6	−588.0	2.8	−622.5
$V(F_2)$	−198.739 402	−199.665 641	−0.46	−198.734 278	−199.669 545	−0.47	−199.366 961
V'	0.00	−0.4873	···	0.5365	0.00	···	−0.0044
V''	8.818	8.217	7.3	5.365	4.703	14.1	4.778
V'''	−54.95	−56.24	−2.3	−36.18	−36.39	−0.6	−34.99
V''''	302.3	311.9	−3.1	194.7	211.3	−7.9	176.8

[a]See footnotes a–c of Table II.

W. D. Allen, A. G. Császár, *J. Chem. Phys.* 98 (1993) 2983.

I. Tailor-made approach: prederived, analytic, case-dependent *T*, unique code for each molecule

The simplest grid-based procedure to solve the (triatomic) rovibrational problem variationally:

The D^3OPI and D^2FOPI algorithms

Discrete Variable Representation of the Hamiltonian

Energy operator in orthogonal (**O**) coordinate system

Direct-product (**P**) basis

Diagonalization with an iterative (**I**) technique (*e.g.*, Lánczos)

G. Czakó, T. Furtenbacher, A. G. Császár, and V. Szalay, *Mol. Phys.* (*Nicholas C. Handy Special Issue*) **102**, 2411 (2004).
T. Szidarovszky, A. G. Császár, and G. Czakó, *PCCP* **12**, 8373 (2010).

II. General Hamiltonian: DEWE

(Discrete Variable Representation – Eckart-Watson Hamiltonian – Exact inclusion of the potential energy)

1. Eckart-Watson vibrational operator (normal coordinates: Eckart-system, orthogonal, rectilinear internal coordinates):

$$\hat{H} = \frac{1}{2}\sum_{\alpha\beta}\hat{\pi}_\alpha\,\mu_{\alpha\beta}\,\hat{\pi}_\beta - \frac{\hbar^2}{8}\sum_{\alpha}\mu_{\alpha\alpha} + \frac{1}{2}\sum_{k=1}^{3N-6}\hat{P}^2 + V$$

2. Numerically exact inclusion of arbitrary (*e.g.*, valence) coordinate potential energy surface

$$\mathbf{r}_{pi} = \mathbf{C}\left[\mathbf{c}_i - \mathbf{c}_p + \sum_{k=1}^{3N-6}\left(\frac{1}{\sqrt{m_i}}\mathbf{l}_{ik} - \frac{1}{\sqrt{m_p}}\mathbf{l}_{pk}\right)Q_k\right]$$

3. Matrix of Hamiltonian in DVR representation, on-the-fly (impossible to store even the nonzero elements of the sparse Hamiltonian) iterative eigenvalue and eigenvector computation (Lanczos).

E. Mátyus, G. Czakó, B. T. Sutcliffe, A. G. Császár, *J. Chem. Phys.* **127**, 084102 (2007).

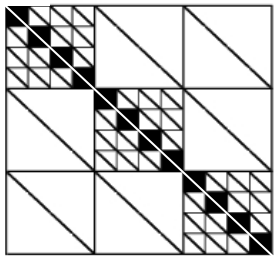
E. Mátyus, J. Šimunek, A. G. Császár, *J. Chem. Phys.* **131**, 074106 (2009).

DEWE

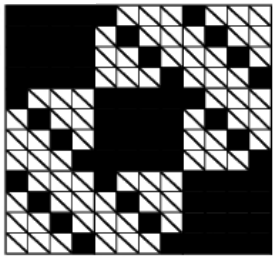
(Discrete Variable Representation – Eckart–Watson Hamiltonian – Exact inclusion of the potential energy)

3. a) Direct-product basis ($N = n^D$, $D = 3N$-6). For example, $D = 3$

$$\boldsymbol{\pi}_\alpha \sim \mathrm{O}\left(N^{1+\frac{1}{D}}\right)$$



$$\mathbf{H} \sim \mathrm{O}\left(N^{1+\frac{2}{D}}\right)$$



3. b) In iterative „diagonalization" algorithms explicit knowledge of **H** is not needed, enough to form $\mathbf{y}^{\mathrm{Lanczos}} = \mathbf{H}\mathbf{x}^{\mathrm{in}}$:

$$\mathbf{y}^{\mathrm{Lanczos}} = \left(\sum_{\alpha\beta} \boldsymbol{\pi}_\alpha\, \boldsymbol{\mu}_{\alpha\beta}\, \boldsymbol{\pi}_\beta\right)\mathbf{x}^{\mathrm{in}} = \sum_{\alpha\beta}\left(\boldsymbol{\pi}_\alpha\left(\boldsymbol{\mu}_{\alpha\beta}\left(\boldsymbol{\pi}_\beta\, \mathbf{x}^{\mathrm{in}}\right)\right)\right)$$

On-the-fly computation of Hamilton-matrix – Lánczos vector multiplication.

E. Mátyus, G. Czakó, B. T. Sutcliffe, A. G. Császár, *J. Chem. Phys.* **127**, 084102 (2007).

E. Mátyus, J. Šimunek, A. G. Császár, *J. Chem. Phys.* **131**, 074106 (2009).

Vibrational Subspace (VS) technique

$$\hat{H} = \frac{1}{2}\sum_{k=1}^{3N-6} \hat{P}_k^2 + \frac{1}{2}\sum_{\alpha,\beta}(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}(\hat{J}_\beta - \hat{\pi}_\beta) - \frac{\hbar^2}{8}\sum_{\alpha}\mu_{\alpha\alpha} + \hat{V}$$

$$\hat{H} = \hat{T}^{\mathrm{v}} + \hat{T}^{\mathrm{r}} + \hat{T}^{\mathrm{r}v} + \hat{V} = \hat{H}^{\mathrm{v}} + \hat{T}^{\mathrm{r}} + \hat{T}^{\mathrm{r}v}$$

$$\hat{H}^{\mathrm{v}} = \hat{T}^{\mathrm{v}} + \hat{V}$$

$$\hat{H}^{\mathrm{v}}\phi_i = E_i\phi_i$$

$$\Psi_i = \sum_{j=1}^{n}\sum_{k=1}^{2J+1} c_{jk}^{i}\phi_j R_k$$

III. GENIUSH: General rovib code with Numerical, Internal-Coordinate, User-Specified Hamiltonians

(general code – full- of reduced-dimensional rovibrational problem – internal coordinate Hamiltonian with numerical computation of both T and V – discrete variable representation)

$$\hat{T}^{\mathrm{rv}} = \frac{1}{2}\sum_{k=1}^{D+3}\sum_{l=1}^{D+3} \tilde{g}^{-1/4}\hat{p}_k^{\dagger} G_{kl}\tilde{g}^{1/2}\hat{p}_l\tilde{g}^{-1/4}$$

$$\hat{H}^{\mathrm{rv}} = \hat{T}^{\mathrm{rv}} + \hat{V} = \hat{T}^{\mathrm{vib}} + \hat{T}^{\mathrm{rot}} + \hat{T}^{\mathrm{rotvib}} + \hat{V}$$

$$\hat{T}^{\mathrm{vib}} = \frac{1}{2}\sum_{k=1}^{D}\sum_{l=1}^{D} \tilde{g}^{-1/4}\hat{p}_k^{\dagger} G_{kl}\tilde{g}^{1/2}\hat{p}_l\tilde{g}^{-1/4}$$

$$\hat{T}^{\mathrm{rot}} = \frac{1}{2}\sum_{k=1}^{3} G_{k+D,k+D}\,\hat{J}_k^2 + \frac{1}{2}\sum_{k=1}^{3}\sum_{l>k}^{3} G_{k+D,l+D}\,[\hat{J}_k, \hat{J}_l]_+$$

$$\hat{T}^{\mathrm{rotvib}} = \frac{1}{2}\sum_{l=1}^{3}\sum_{k=1}^{D}\left(\tilde{g}^{-1/4}\hat{p}_k^{\dagger} G_{k,l+D}\,\tilde{g}^{1/4} + \tilde{g}^{1/4} G_{k,l+D}\,\hat{p}_k\tilde{g}^{-1/4}\right)\hat{J}_l$$

E. Mátyus, G. Czakó, A. G. Császár, *J. Chem. Phys.* **130**, 134112 (2009).

C. Fábri, E. Mátyus, A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).

GENIUSH

Initial specifications

- body-fixed frame (*e.g.*, Eckart, principal axis, „xxy" gauge)
- set of internal coordinates (*e.g.*, *Z*-matrix, Radau)
- constraints for the coordinates if necessary
- Cartesian coordinates of the atoms

„Main" program

- numerical or analytical 1st, 2nd, and 3rd derivatives of Euler angles and internal coordinates in terms of Cartesians and vice versa
- numerically compute **G** matrix, U, and V at every grid point
- determine needed eigenpairs via variants of Lanczos' algorithm(s)

Result: single code for all full- or reduced-dimensionality problems for molecules with arbitrary number of "interacting" minima

E. Mátyus, G. Czakó, A. G. Császár, *J. Chem. Phys.* **130**, 134112 (2009).

C. Fábri, E. Mátyus, A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).

A system with two "interacting" minima: NH_3

Table 2: Internal coordinates of NH_3: $r_1, r_2, r_3, \theta, \beta_1, \beta_2$.

N						
X	N	1.0				
H1	N	r_1	X	θ		
H2	N	r_2	X	θ	H1	β_1
H3	N	r_3	X	θ	H1	β_2

Full- and reduced-D models for NH_3 motions

VBO					6-D	Expt.
$0^+(A_1')$					7436.82	…
$0^-(A_2'')$					0.79	0.79
$\nu_2^+(A_1')$					932.41	932.43
$\nu_2^-(A_2'')$					968.15	968.12
$2\nu_2^+(A_1')$					1597.26	1597.47
$\nu_4^+(E')$					1625.62	1626.28
$\nu_4^-(E'')$					1626.73	1627.37
$2\nu_2^-(A_2'')$					1882.18	1882.18

C. Fábri, E. Mátyus, A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).

Full- and reduced-D models for NH_3 motions

VBO	1-D				6-D	Expt.
$0^+(A_1')$	521.43				7436.82	…
$0^-(A_2'')$	1.13				0.79	0.79
$\nu_2^+(A_1')$	930.57				932.41	932.43
$\nu_2^-(A_2'')$	979.80				968.15	968.12
$2\nu_2^+(A_1')$	1586.97				1597.26	1597.47
$\nu_4^+(E')$	…				1625.62	1626.28
$\nu_4^-(E'')$	…				1626.73	1627.37
$2\nu_2^-(A_2'')$	1918.86				1882.18	1882.18

C. Fábri, E. Mátyus, A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).

Reduced- and full-D models for NH_3 motions

VBO	1-D	2-D	3-D	4-D	6-D	Expt.
$0^+(A_1')$	521.43	2256.74	2158.70	3911.34	7436.82	…
$0^-(A_2'')$	1.13	1.28	1.70	1.74	0.79	0.79
$\nu_2^+(A_1')$	930.57	900.48	904.48	881.01	932.41	932.43
$\nu_2^-(A_2'')$	979.80	952.80	970.68	946.02	968.15	968.12
$2\nu_2^+(A_1')$	1586.97	1537.60	1550.06	1511.43	1597.26	1597.47
$\nu_4^+(E')$	…	…	1659.43	1649.71	1625.62	1626.28
$\nu_4^-(E'')$	…	…	1662.12	1652.08	1626.73	1627.37
$2\nu_2^-(A_2'')$	1918.86	1868.39	1917.98	1867.66	1882.18	1882.18

C. Fábri, E. Mátyus, A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).

Some “fourth-age” challenges

(1) Determination of a full (truly global) accurate PES for many-electron systems (no refinement of the PES is needed)

(2) Doing nuclear motion calculations close to (below and above) the dissociation asymptotes

(3) Handling of nonadiabaticity and cases with several surfaces

(4) Getting away from fitting of PESs

(5) Treatment(s) without the Born-Oppenheimer approximation

(6) Effective extension of accurate nuclear motion computation to many more dimensions (atoms)

The 23rd Colloquium on High Resolution Molecular Spectroscopy

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