

Diagonalization, eigenvalues problem, secular equation

Diagonalization procedure of a matrix A with dimensionality $n \times n$ (e.g. the Hessian matrix)

$$A = \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix}$$

consists in finding a matrix C such, that the matrix $D=C^{-1}AC$ is diagonal:

$$C^{-1}AC = D = \begin{bmatrix} d_1 & 0 & \dots & 0 \\ 0 & d_2 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & d_n \end{bmatrix}$$

Equation $C^{-1}AC=D$ can also be written as

$$AC = CD$$

Denoting the elements of matrix C by c_{ij} and using the fact that D is diagonal (i.e., its elements d_{ij} are of the form $d_j\delta_{ij}$, where δ_{ij} denotes the Kronecker delta, $\delta_{ii}=1$ and $\delta_{ij}=0$ for $i \neq j$) we obtain

$$(AC)_{ij} = \sum_k a_{ik} c_{kj} \qquad (CD)_{ij} = \sum_k c_{ik} d_{kj} = \sum_k c_{ik} d_j \delta_{kj} = d_j c_{ij}$$

Diagonalization, eigenvalues problem, secular equation

Employing the equation $(AC)_{ij} = (CD)_{ij}$ we obtain

$$\sum_k a_{ik} c_{kj} = d_j c_{ij}$$

In matrix notation this equation takes the form

$$A C_j = d_j C_j$$

where C_j is the j th column of matrix C . This is equation for the eigenvalues (d_j) and eigenvectors (C_j) of matrix A . Solving this equation, that is the solving the so called eigenproblem for matrix A , is equivalent to diagonalization of matrix A . This is because the matrix C is built from the (column) eigenvectors C_1, C_2, \dots, C_n :

$$C = [C_1, C_2, \dots, C_n]$$

The equation for eigenvectors can also be written as $(A - d_j E) C_j = 0$, where E is the unit matrix with elements δ_{ij} . This equation has a solution only if the determinant of the matrix $A - d_j E$ vanishes

$$|A - d_j E| = 0$$

This is the very important and practically useful secular equation for eigenvalues d_j .

Hartree-Fock Theory

The wave function Φ in the Hartree-Fock theory is a **Slater determinant**

$$\Phi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix}$$

built from **molecular spinorbitals** $\phi_k(i) = \phi_k(\vec{r}_i, \sigma_i) = \phi_k(x_i, y_i, z_i, \sigma_i)$. Symbolically:

$$\Phi = | \phi_1 \phi_2 \phi_3 \dots \phi_N |$$

Molecular spinorbitals ϕ_i are determined by minimalization of the **energy functional**:

$$\mathcal{E}[\Phi] = \int \Phi^* \hat{H} \Phi d\tau$$

where \hat{H} is the **electronic Hamiltonian** of a molecule.



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VLADIMIR A. FOCK

Born on December 22, 1898. Professor of Physics, University of Leningrad (U.R.S.S.).

Member of the Academy of Sciences of the Soviet Union. Member of the Academies of Sciences of Germany, Norway and Denmark.

Author of:

"Principles of wave-mechanics", "The theory of Space, Time and Gravitation", "Electromagnetic Diffraction and Propagation Problems".



Important Contributions:

Relativistic equation of wave-mechanics (Klein–Fock equation, 1926). Dirac equation and Riemann geometry (1929). Hartree–Fock method (1930). Quadridimensionnal symmetry of hydrogen atom (1935). Quantum field theory (Fock space, Fock representation 1932–1937). Gravitation theory (1939–1950). Propagation of electromagnetic waves (1944–1965). Epistemological research on the theory of relativity

Hartree-Fock Theory, continued

- RHF (Restricted Hartree-Fock) Method

For 6 electrons it is sufficient to use 3 or 4 orbitals: $\psi_1, \psi_2, \psi_3, \text{ i } \psi_4$

Singlet states: $\Phi = | \psi_1\alpha \psi_1\beta \psi_2\alpha \psi_2\beta \psi_3\alpha \psi_3\beta |$

Triplet states: $\Phi = | \psi_1\alpha \psi_1\beta \psi_2\alpha \psi_2\beta \psi_3\alpha \psi_4\alpha |$

(because of double occupancy of orbitals).

- UHF (Unrestricted Hartree-Fock) Method

For 6 electrons one has to use 6 orbitals:

Singlet state: $\Phi = | \psi_1\alpha \psi'_1\beta \psi_2\alpha \psi'_2\beta \psi_3\alpha \psi'_3\beta |$

Triplet state: $\Phi = | \psi_1\alpha \psi'_1\beta \psi_2\alpha \psi'_2\beta \psi_3\alpha \psi_4\alpha |$

(because different orbitals for different spins are used)

Both methods are employed in practice. Both have advantages and disadvantages.

The RHF method is simpler, gives a state of a well defined, pure spin, but fails to correctly describe chemical bond dissociation.

The UHF is more time-consuming, correctly describes chemical bond dissociation, but gives states of undefined spin (spin contamination) and (often) artifacts on potential energy surfaces.

Hartree-Fock equations

$$\hat{f}\phi_k = \varepsilon_k\phi_k$$

where ε_k is the so-called **orbital energy** and \hat{f} is the **Fock operator**

$$\hat{f} = \hat{h} + \hat{J} - \hat{K}$$

\hat{h} denotes the sum of the kinetic energy operator and the attractive nuclear potential:

$$\hat{h} = -\frac{1}{2}\Delta - \sum_j \frac{Z_j}{|\vec{r} - \vec{R}_j|}$$

The **Coulomb** \hat{J} and **exchange** \hat{K} operators are more complicated. The Coulomb operator \hat{J} depends linearly on the **electron density** $\rho(\vec{r})$ defined as :

$$\rho(\vec{r}, \sigma) = \sum_k^{\text{occ}} \phi_k^2(\vec{r}, \sigma)$$

In particular \hat{J} represents the multiplication by the averaged potential $j(\vec{r})$ of the electron cloud:

$$j(\vec{r}) = \int \frac{1}{|\vec{r} - \vec{r}'|} \rho(\vec{r}') d\vec{r}' \quad (1)$$

Hartree-Fock equations, continued

The exchange operator \hat{K} is more complicated. This is an integral operator depending on all occupied orbitals:

$$(\hat{K}\psi)(\vec{r}) = \sum_k^{\text{occ}} \int \phi_k(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \psi(\vec{r}') d\vec{r}' \phi_k(\vec{r}) \quad (2)$$

(you do not have to memorize this formula).

The Hartree-Fock energy E_{HF} is computed in the following way:

$$E_{\text{HF}} = \int \Phi \hat{H} \Phi d\tau = \sum_i \epsilon_i - \frac{1}{2} \sum_k (J_{kk} - K_{kk}) \quad (3)$$

where

$$J_{kk} = \int \phi_k \hat{J} \phi_k d\tau \quad K_{kk} = \int \phi_k \hat{K} \phi_k d\tau \quad (4)$$

are the *Coulomb* and *exchange* integrals, respectively.

Very important in applications is **the Koopmans theorem** concerning the ionization potential (IP) and the electron affinity (EA) of an atom or a molecule:

$$\text{IP.} = -\epsilon_{\text{HOMO}}$$

$$\text{EA} = \epsilon_{\text{LUMO}}$$

where HOMO denotes the *highest occupied* and LUMO the *lowest unoccupied molecular orbital* (MO).

LCAO MO Method. Roothaan Equations

In the LCAO MO method the molecular spinorbitals are represented as linear combinations of atomic **spinorbitals** $\chi_j(\vec{r}, \sigma)$:

$$\phi_k(\vec{r}, \sigma) = \sum_{j=1}^{2M} C_{jk} \chi_j(\vec{r}, \sigma)$$

Spinorbitals χ_j **are not** exact atomic spinorbitals but to a large extent arbitrary functions (basis functions) localized on atomic centers in a molecule.

In particular, the functions χ_j are expressed through M functions (orbitals) of an atomic basis $b_j(\vec{r})$:

$$\chi_{2j-1}(\vec{r}, \sigma) = b_j(\vec{r})\alpha(\sigma) \qquad \chi_{2j}(\vec{r}, \sigma) = b_j(\vec{r})\beta(\sigma)$$

The choice of the atomic basis $b_j(\vec{r})$ and its size M determine the accuracy of calculations.

The linear coefficients C_{jk} and orbital energies ε_k are found by solving the **Roothaan equations**:

$$FC_k = \varepsilon_k SC_k$$

where F is the **Fock matrix**, S is the **overlap matrix**, and C_k is the k th column of matrix C

$$F_{ij} = \int \chi_i^* \hat{f} \chi_j d\tau \qquad S_{ij} = \int \chi_i^* \chi_j d\tau$$



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CLEMENS C. J. ROOTHAAN

Born August 29, 1918 in Nymegen, Netherlands.

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Clemens Roothaan was educated at the Technical Institute Delft (MS 1945) and at the University of Chicago (PhD, Physics 1950). He was Research Associate (1949–50), Instructor to Professor of Physics and Chemistry (1950–), Professor of Communications and Information Science (1965–68), Director of the Computer Center (1962–68), at the University of Chicago.

He was also Guggenheim Fellow, Cambridge University (1957), Consultant for : Argonne National Laboratory (1958-66), Lockheed Missiles and Space Company (1960-65), Union Carbide Corporation (1965-), IBM Corporation (1965-). He has been Visiting Professor at the Ohio State University (1976), the Technical University, Lyngby, Denmark (1983), University of Delft (1987-88).



The SCF Method

In practice the Roothaan equations $FC_k = \varepsilon_k SC_k$ are solved iteratively.

In the n th iteration we diagonalize the Fock matrix F computed using the orbitals from the $(n - 1)$ th iteration.

The most time-consuming step is the calculation of $M^4/8$ two-electron integrals (including four-center ones):

$$\langle pq|rs\rangle = \iint b_p^*(\vec{r}_1) b_q^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} b_r(\vec{r}_1) b_s(\vec{r}_2) d\tau_1 d\tau_2$$

needed to form the Fock matrix F (remember that $\hat{f} = \hat{h} + \hat{J} - \hat{K}$).

The choice of the atomic basis $b_j(\vec{r})$ and its size M determine the accuracy of calculations.

Each kind of an atom requires different basis. Up to now hundreds of basis sets have been developed.

Initially **Slater basis sets**, mainly **minimal Slater bases** were used:

$$S_{nlm}(\vec{r}) = r^{n-l} e^{-\zeta r} Y_{lm}(\theta, \phi)$$

For instance, for atoms Li to Ne, the minimal basis (MBS) consists of only 5 functions:

$$1s = e^{-\zeta r} \quad 2s = r e^{-\zeta r} \quad 2p_x = x e^{-\zeta r} \quad 2p_y = y e^{-\zeta r} \quad 2p_z = z e^{-\zeta r}$$

Gaussian Bases

In 1950 **Frank Boys** made a breakthrough discovery. He observed that the product of Gaussian functions, $e^{-\gamma r^2}$, localized on different atoms is again a Gaussian function (localized at a point between them).

Due to this property **all two-electron integrals, including the four-center ones are expressible through very simple, closed form formulas and can be quickly computed.**

Boys proposed to use in SCF calculations the Gaussian basis functions of the following general form:

$$G_{pqS}(\vec{r}) = x^p y^q z^s e^{-\gamma r^2}$$

In particular, the $1s$ i $2p$ Gaussian functions are of the form:

$$1s = e^{-\gamma r^2} \quad 2p_x = x e^{-\gamma r^2} \quad 2p_y = y e^{-\gamma r^2} \quad 2p_z = z e^{-\gamma r^2}$$

There are two kinds of d functions. We use either the **5 spherical Gaussian functions** :

$$G_{3d,m}(\vec{r}) = r^2 e^{-\gamma r^2} Y_{2m}(\theta, \phi)$$

or the **6 Cartesian ones**

$$d_{x^2} = x^2 e^{-\gamma r^2} \quad d_{y^2} = y^2 e^{-\gamma r^2} \quad d_{z^2} = z^2 e^{-\gamma r^2} \quad d_{xy} = xy e^{-\gamma r^2} \quad d_{xz} = xz e^{-\gamma r^2} \quad d_{yz} = yz e^{-\gamma r^2}$$

The Gaussian functions of the type $2s$, $3p$, $4d$, etc, (with odd powers of r) are not used.



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SAMUEL F. BOYS

Born 20 December 1911 in Pudsey, Yorkshire, England. Died 16 October 1972 in Cambridge, England. Reader in Theoretical Chemistry, University of Cambridge.

Fellow of the Royal Society of London, 1972.

Author of:

36 scientific papers.

Important Contributions:

His contributions to Quantum Molecular Science are all fundamental. He introduced Gaussian functions for molecular wavefunction calculations (1950), in particular showing the evaluation of 4-centre integrals. He favoured Configuration Interaction, and evaluated the necessary matrix elements. He predicted the future for computational chemistry (Nature, 1956). He calculated the ground state of CH_2 to be a triplet (129°), followed by the (almost linear) singlet, 0.04 au higher. (1960). Both predictions were later confirmed. He introduced localised (oscillator) orbitals for formaldehyde (1960). The transcorrelated



S. F. Boys

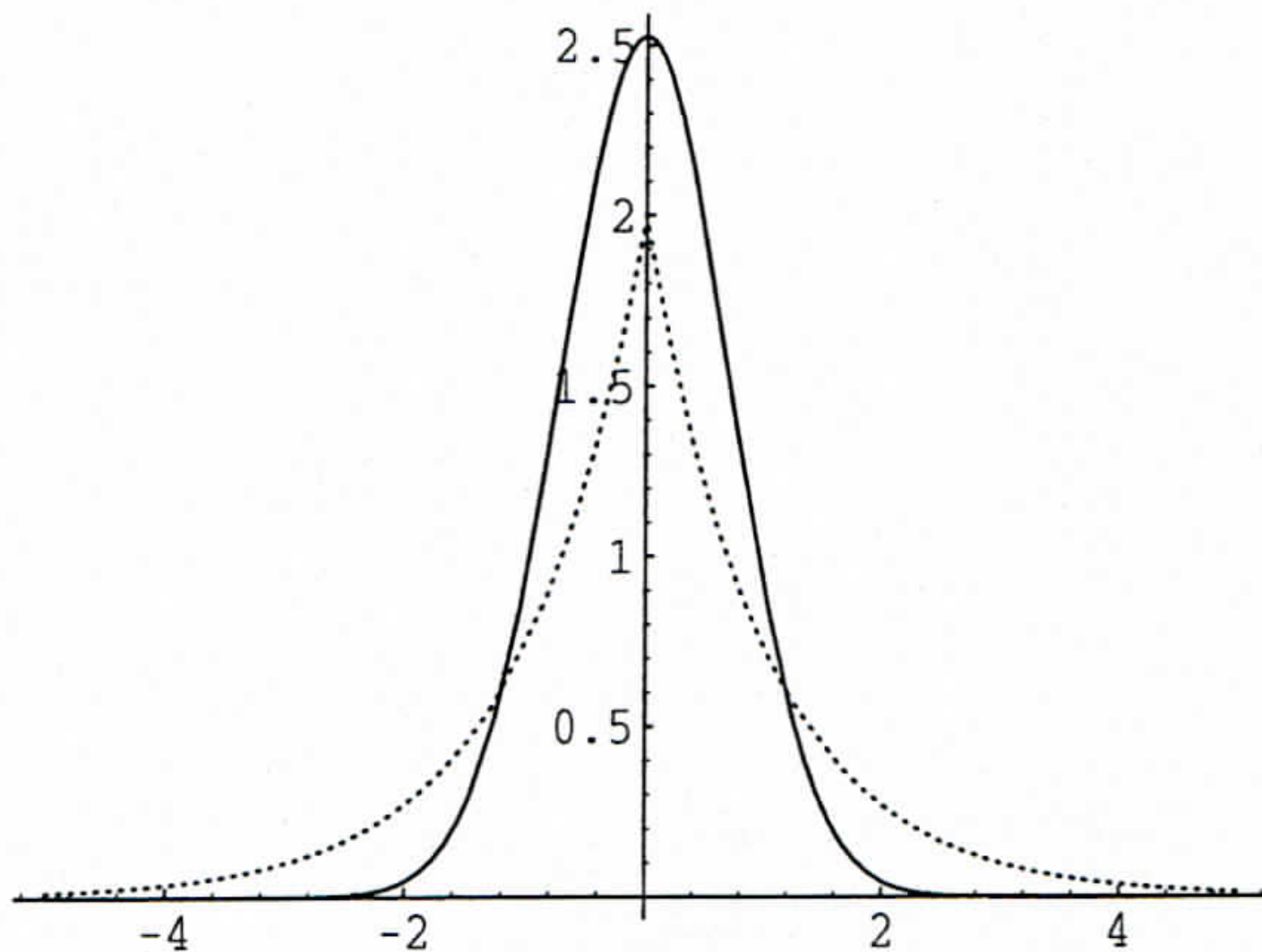


Fig. 4. Unit exponent normalized GTO and STO. Solid line: GTO; Dashed line: STO.

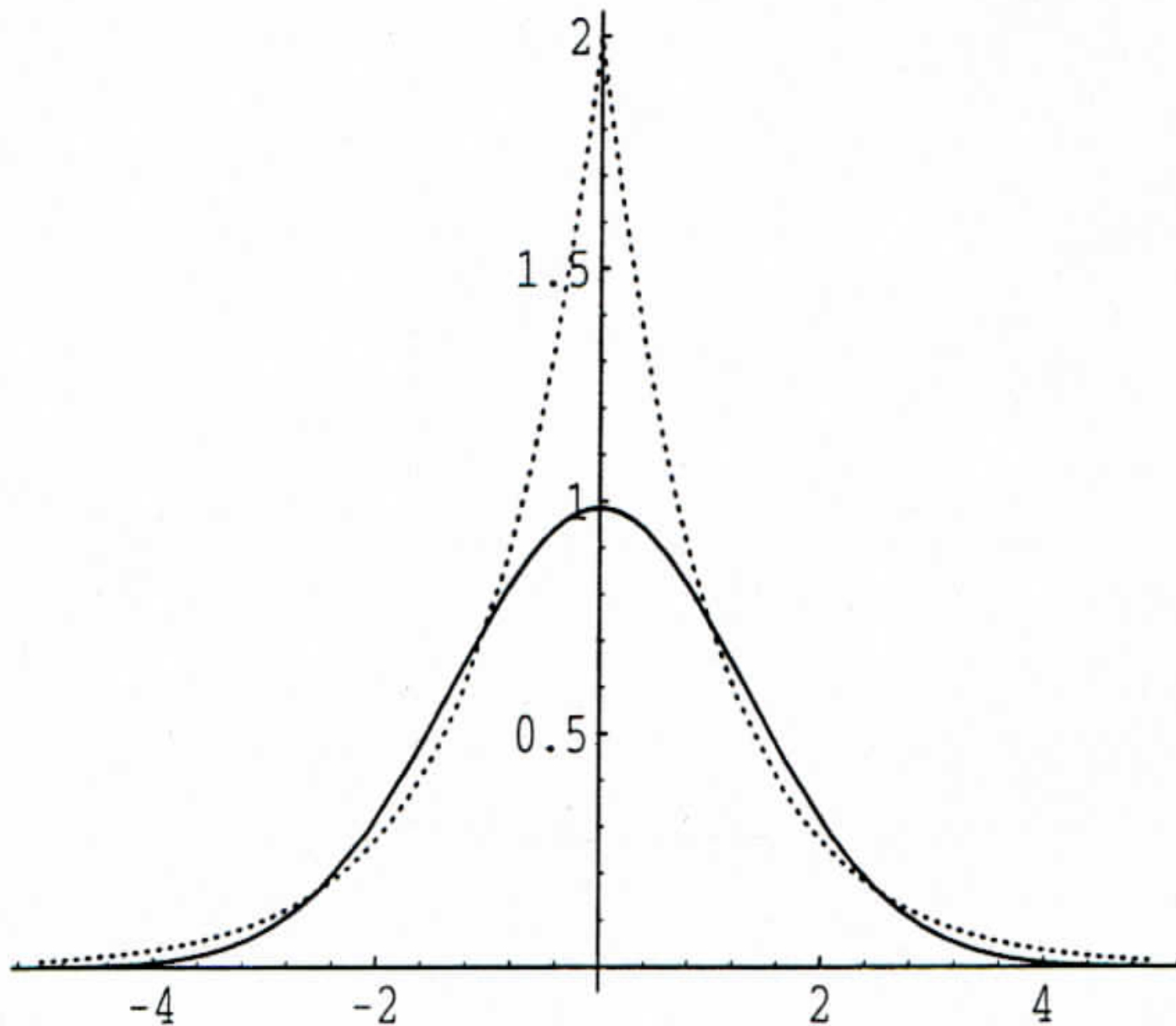


Fig. 5. Optimum GTO for H 1s. Solid line: GTO; Dashed line: STO.

Hierarchy of Gaussian Bases (1)

To correct the wrong behavior of Gaussian functions at small r one uses **contracted bases**.

$$c_j(\vec{r}) = \sum_{n=1}^K c_{nj} e^{-\gamma_{nj} r^2}$$

where $e^{-\gamma_{nj} r^2}$ are the so-called **primitive functions**, c_{nj} are the **contraction coefficients**, and $c_j(\vec{r})$ is the K -term **contracted function**.

The contraction coefficients c_{nj} are chosen such that $c_j(\vec{r})$ optimally approximates Slater orbitals.

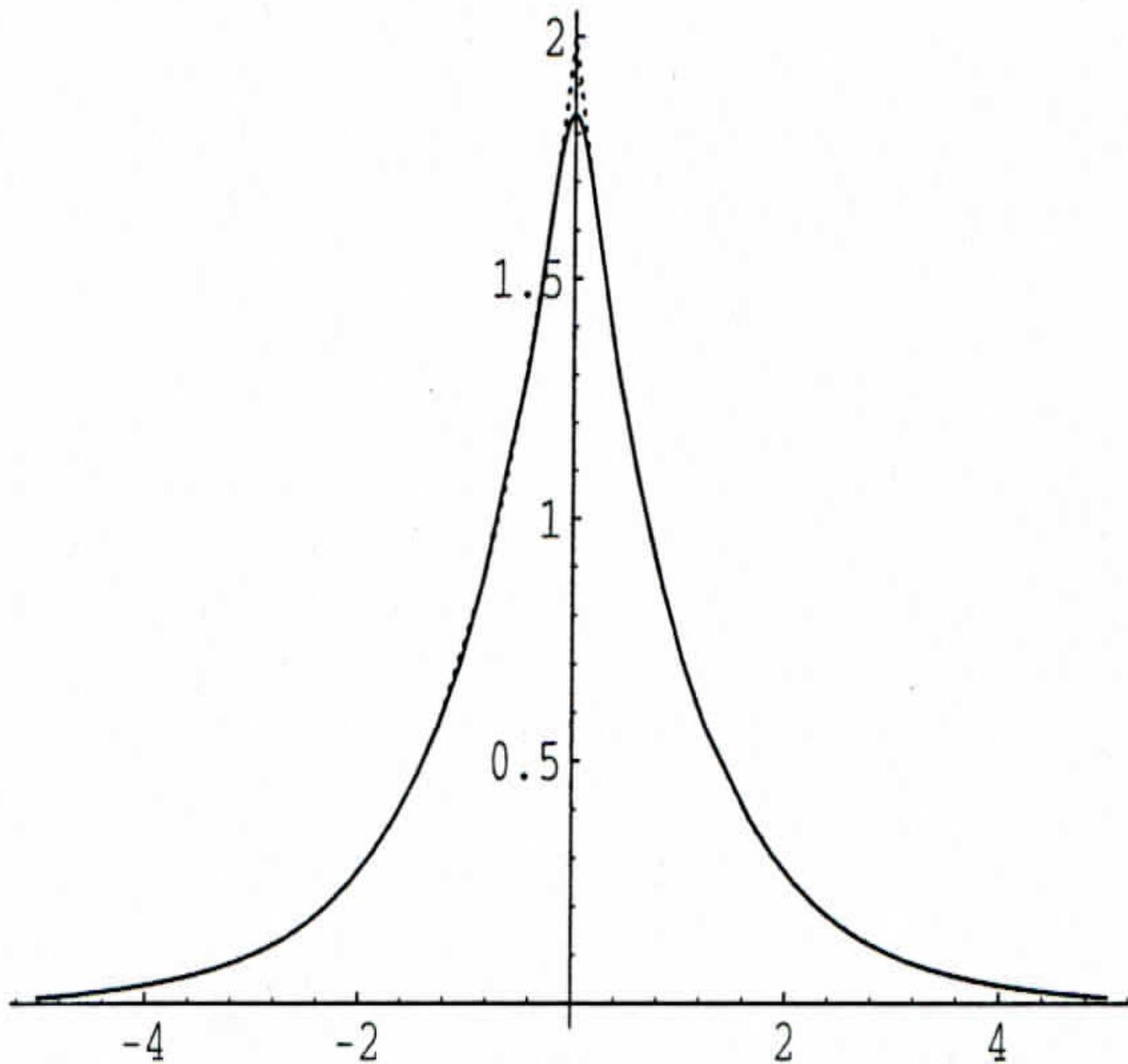


Fig. 6. Four-term GTO expansion for H 1s. Solid line: GTO; Dashed line: STO.

Hierarchy of Gaussian Bases (2)

To correct the wrong behavior of Gaussian functions at small r one uses **contracted bases**.

$$c_j(\vec{r}) = \sum_{n=1}^K c_{nj} e^{-\gamma_{nj} r^2}$$

where $e^{-\gamma_{nj} r^2}$ are the so-called **primitive functions**, c_{nj} are the **contraction coefficients**, and $c_j(\vec{r})$ is the K -term **contracted function**.

The contraction coefficients c_{nj} are chosen such that $c_j(\vec{r})$ optimally approximates Slater orbitals.

Examples of contracted **minimal bases**: (2s1p bases for atoms Li through Ne:

$K=3 \rightarrow$ STO-3G

$K=4 \rightarrow$ STO-4G

$K=5 \rightarrow$ STO-5G

Using the STO-3G basis Boys obtained $\theta=129^\circ$ for the CH_2 radical contradicting Herzberg's experimental (spectroscopic) determination $\theta=180^\circ$.

Using also the STO-3G basis Pople obtained very good structural prediction for C_4H_6

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GERHARD HERZBERG

Born December 25th, 1904, Hamburg, Germany.

Frederic Ives Medal and Honorary Member of the Optical Society of America. Honorary Fellow and Faraday Medal of the Royal Society of Chemistry. Nobel Prize. Earle K. Plyler Prize of the American Physical Society. Fellow of the Royal Society of London, Bakerian Lecture and Royal Medal. Foreign Associate of the National Academy of America. Honorary Member of the Japan Academy. Foreign Member of the American Philosophical Society.



Author of:

"Atomic Spectra and Atomic Structure"

"Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules"

"Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules"

"Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules"

"Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules"

"The Spectra and Structures of Simple Free Radicals: An introduction to Molecular Spectroscopy"

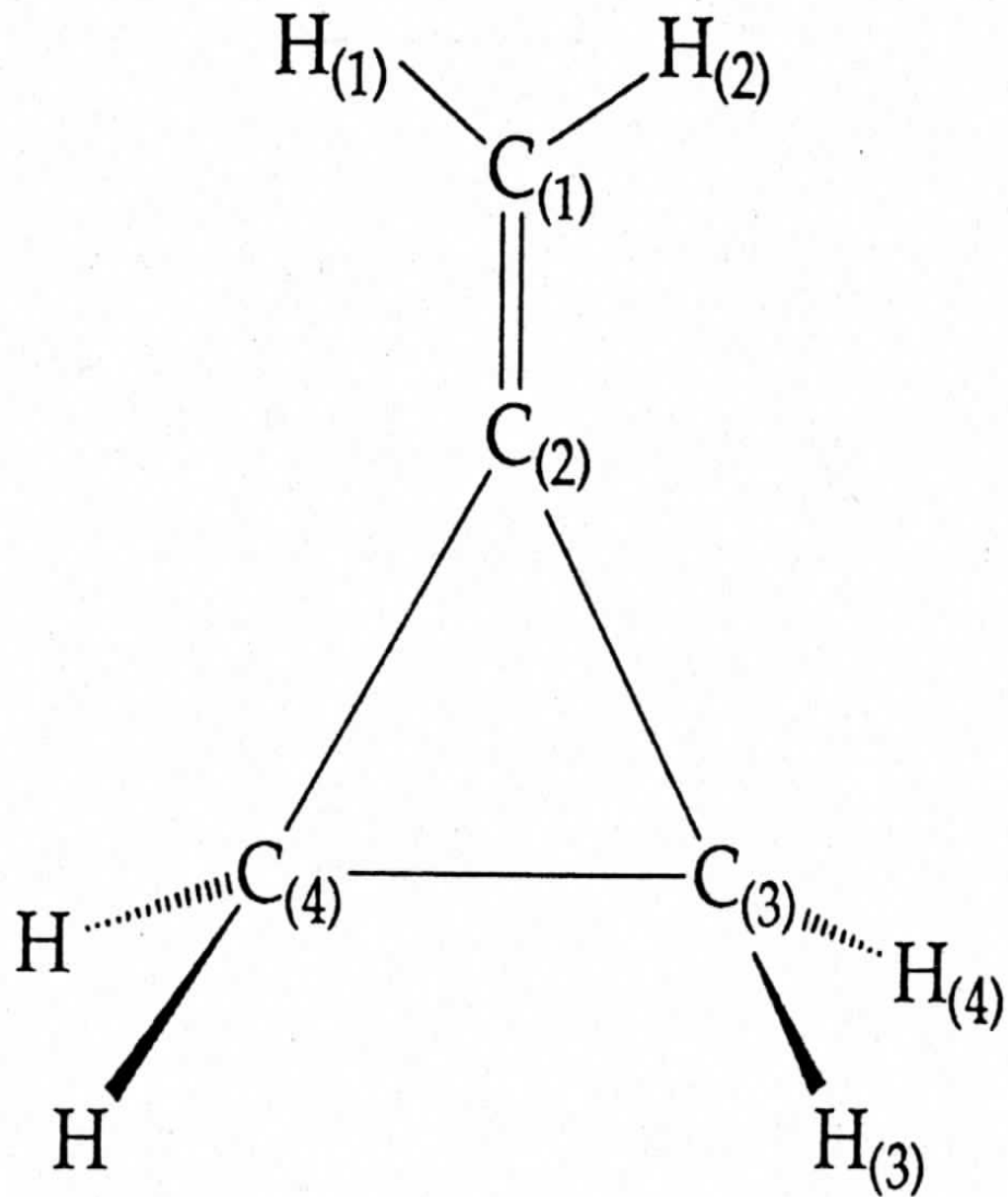


Fig. 3. The methylenecyclopropane molecule (C_{2v} symmetry), for which a complete *ab initio* structure determination was reported in 1975 and is seen in Table 3.

Table 3. Minimum basis set (MBS) self-consistent-field (SCF) geometry prediction compared with experiment for methylenecyclopropane (see Fig. 3).

| Parameter | STO-3G | Experiment |
|---|--------|------------|
| $r_{C_{(1)}=C_{(2)}} (\text{\AA})$ | 1.298 | 1.332 |
| $r_{C_{(2)}-C_{(3)}} (\text{\AA})$ | 1.474 | 1.457 |
| $r_{C_{(3)}-C_{(4)}} (\text{\AA})$ | 1.522 | 1.542 |
| $r_{C_{(1)}-H_{(1)}} (\text{\AA})$ | 1.083 | 1.088 |
| $r_{C_{(3)}-H_{(3)}} (\text{\AA})$ | 1.083 | 1.09 |
| $\theta_{H_{(1)}-C_{(1)}-H_{(2)}} (^{\circ})$ | 116.0 | 114.3 |
| $\theta_{H_{(3)}-C_{(3)}-H_{(4)}} (^{\circ})$ | 113.6 | 113.5 |
| $\theta_{H_{(3)}-C_{(3)}-C_{(4)}} (^{\circ})$ | 149.4 | 150.8 |

Hierarchy of Gaussian Bases (3)

To correct the wrong behavior of Gaussian functions at small r one uses **contracted bases**.

$$c_j(\vec{r}) = \sum_{n=1}^K c_{nj} e^{-\gamma_{nj} r^2}$$

where $e^{-\gamma_{nj} r^2}$ are the so-called **primitive functions**, c_{nj} are the **contraction coefficients**, and $c_j(\vec{r})$ is the K -term **contracted function**.

The contraction coefficients c_{nj} are chosen such that $c_j(\vec{r})$ optimally approximates Slater orbitals.

Examples of contracted **minimal bases**: (2s1p bases for atoms Li through Ne):

$K=3 \rightarrow$ STO-3G

$K=4 \rightarrow$ STO-4G

$K=5 \rightarrow$ STO-5G

Double ζ bases (DZ), (4s2p for atoms Li through Ne).

Polarized bases DZP, TZP, etc. (4s2p1d, 6s3p1d, etc. for atoms Li through Ne) .

Notation:

Basis 4s2p1d (that is the DZP basis) obtained from the contraction of 9 s functions, 5 p functions p and 2 d functions is denoted by **(9s5p2d/4s2p1d)** and its contraction scheme by **[6111/41/2]**

Angle between the OH bonds in the water molecule

| | |
|--------|--------|
| STO-4G | 100° |
| DZ | 113° |
| DZP | 106° |
| TZ2P | 106.3° |
| HF | 106.4° |
| exptl | 104.5° |

Hierarchy of Gaussian Bases (4)

Minimal bases

- STO-3G (6s3p/2s1p)
- STO-4G (8s4p/2s1p)
- STO-5G (10s5p/2s1p)

Double ζ bases

- DZ e.g. (9s5p/4s2p)

Triple ζ bases

- TZ e.g. (11s7p/6s3p)

Polarized bases

- DZP e.g. (9s5p2d/4s2p1d)
- TZP e.g. (11s7p/2d/6s3p1d)
- TZ2P e.g. (11s7p/3d/6s3p2d)

Pople's bases (“Split-valence”)

e.g.. 6-31G that is valence DZ, (10s4p/3s2p) - with contraction [631/31]

Dunning's bases (“correlation consistent (cc)”)

Pople basis sets

- 3-21G
- 3-21G* - Polarized
- 3-21+G - Diffuse functions
- 3-21+G* - With polarization *and* diffuse functions
- 4-21G
- 4-31G
- 6-21G
- 6-31G
- 6-31G*
- 6-31+G*
- 6-31G(3df, 3pd)
- 6-311G
- 6-311G*
- 6-311+G*

The 6-31G* basis set (defined for the atoms H through Zn) is a valence double-zeta polarized basis set that adds to the 6-31G set six *d*-type Cartesian-Gaussian polarization functions on each of the atoms Li through Ca and ten *f*-type Cartesian Gaussian polarization functions on each of the atoms Sc through Zn.



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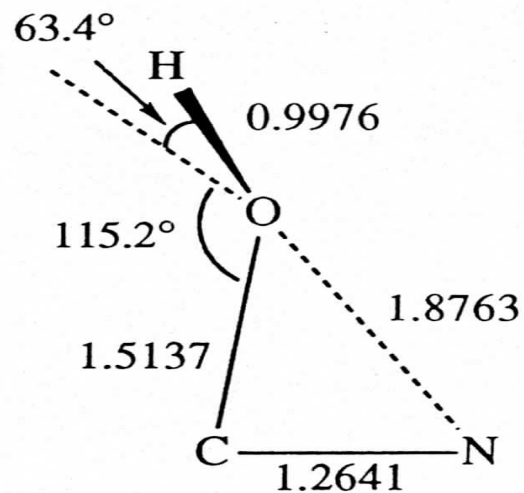
Born October 31, 1925 in England. Trustees Professor of Chemistry, Northwestern University, Evanston, Illinois, USA.

Alexander von Humboldt Foundation, Senior US Scientist Award (1981). G. Willard Wheland Award, University of Chicago (1981). Evans Award, Ohio State University (1982). Oesper Award, University of Cincinnati (1984). Davy Medal, Royal Society, London (1988). Doctor of Science (honoris causa) University of Toronto, Canada (1990). ACS Award for Computers in Science, Atlanta, GA (1991). Max T. Rogers lecturer, Michigan State University, East Lansing, MI (1991). Wolf Prize in Chemistry (1992). Nobel Prize for Chemistry (1998).

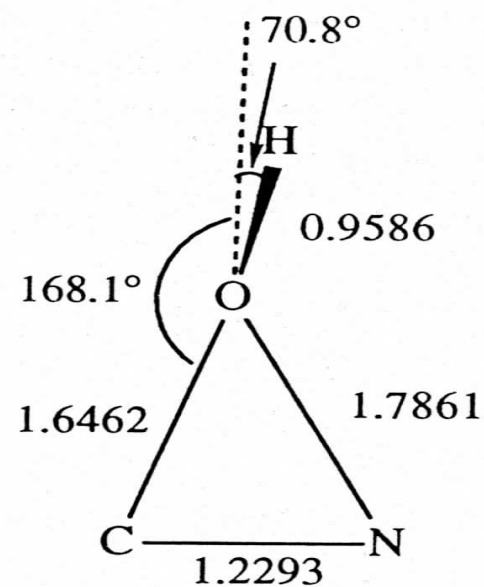


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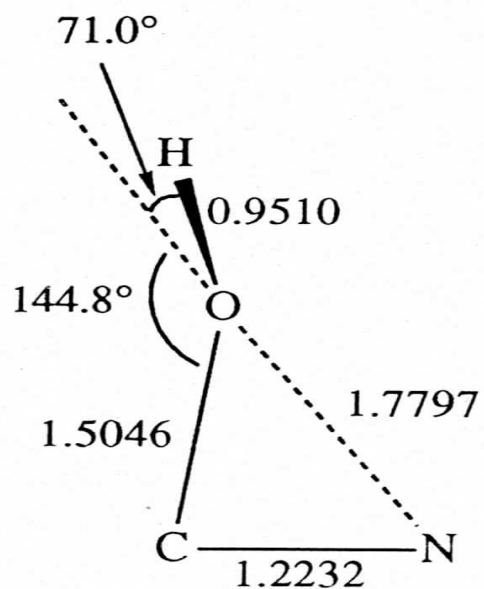
High Resolution Nuclear Magnetic Resonance, J.A. Pople, W. G. Schneider, and H.J. Bernstein (McGraw-Hill, 1959). Approximate Molecular Orbital Theory, J.A. Pople and D.L. Beveridge (McGraw-Hill Series in Advanced Chemistry, 1970). Ab Initio Molecular Orbital Theory, W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, John Wiley and



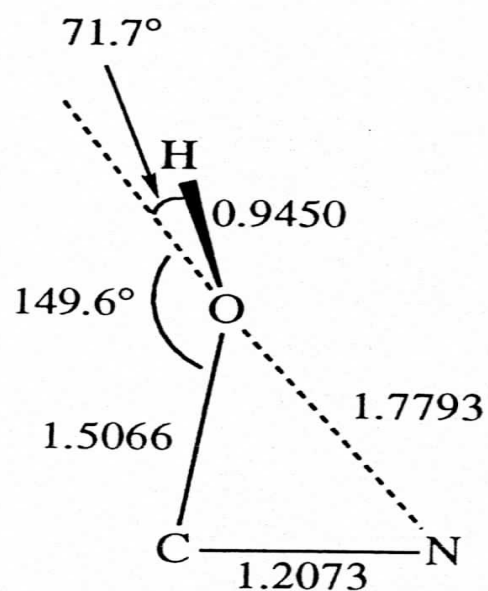
STO-3G



4-31G



DZP



TZ2Pf

Fig. 4. Self-consistent-field predictions of the transition state geometry for the $\text{HONC} \rightarrow \text{HOCN}$ unimolecular rearrangement. Bond distances are in Å. It is seen that in this case the transition state structure is strongly dependent on the basis set chosen.