

# SimMat 2025

Lecture 1:  
Método de Hartree-Fock & DFT-DFA

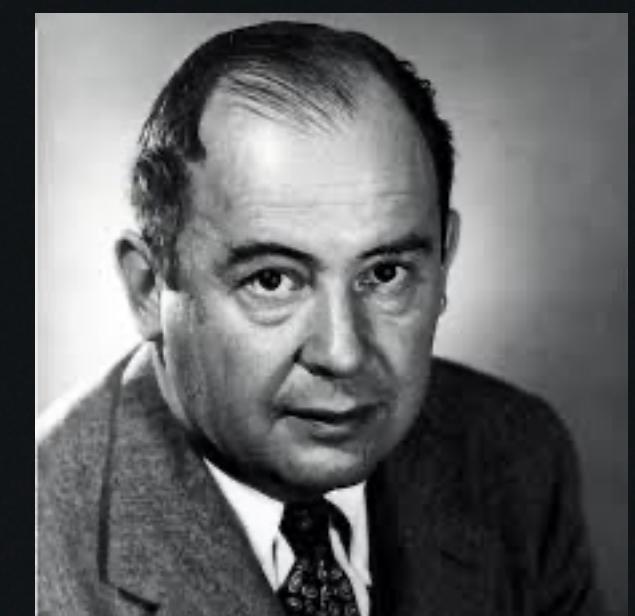
# Hartree-Fock

Una pequeña Introducción

$$f(1)\chi_a(1) = \left[ h(1) + \sum_b \int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_b(2) \right] \chi_a(1)$$

# QM

$$\frac{-\hbar}{i} \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$



$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad \langle \Psi | \Psi \rangle = 1$$

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E = E[|\Psi\rangle]$$

$$\delta(\langle \Psi | \hat{H} | \Psi \rangle - \mu(\langle \Psi | \Psi \rangle - 1)) = 0$$

Problema variacional

QM

$$\hat{H} = \sum_i^N \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{\alpha}^N \left( -\frac{1}{2} \nabla_{\alpha}^2 \right) + \sum_i^N v(\mathbf{r}_i) + \sum_{i < j}^N \frac{1}{r_{ij}} + \sum_{\alpha < \beta}^N \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha \beta}}$$

$$\hat{H} = \sum_i^N \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{\alpha}^N \left( -\frac{1}{2} \nabla_{\alpha}^2 \right) - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i < j}^N \frac{1}{r_{ij}} + \sum_{\alpha < \beta}^N \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha \beta}}$$

# La Aproximación de Born-Oppenheimer



$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{H} = \sum_i^N \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{\alpha}^N \left( -\frac{1}{2} \nabla_{\alpha}^2 \right) + \sum_i^N v(\mathbf{r}_i) + \sum_{i < j}^N \frac{1}{r_{ij}} + \sum_{\alpha < \beta}^N \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}$$

$$\Psi = \Psi_{el}(\{\mathbf{r}_i\}; \{\mathbf{R}_{\alpha}\}) * \Psi_{Nu}$$

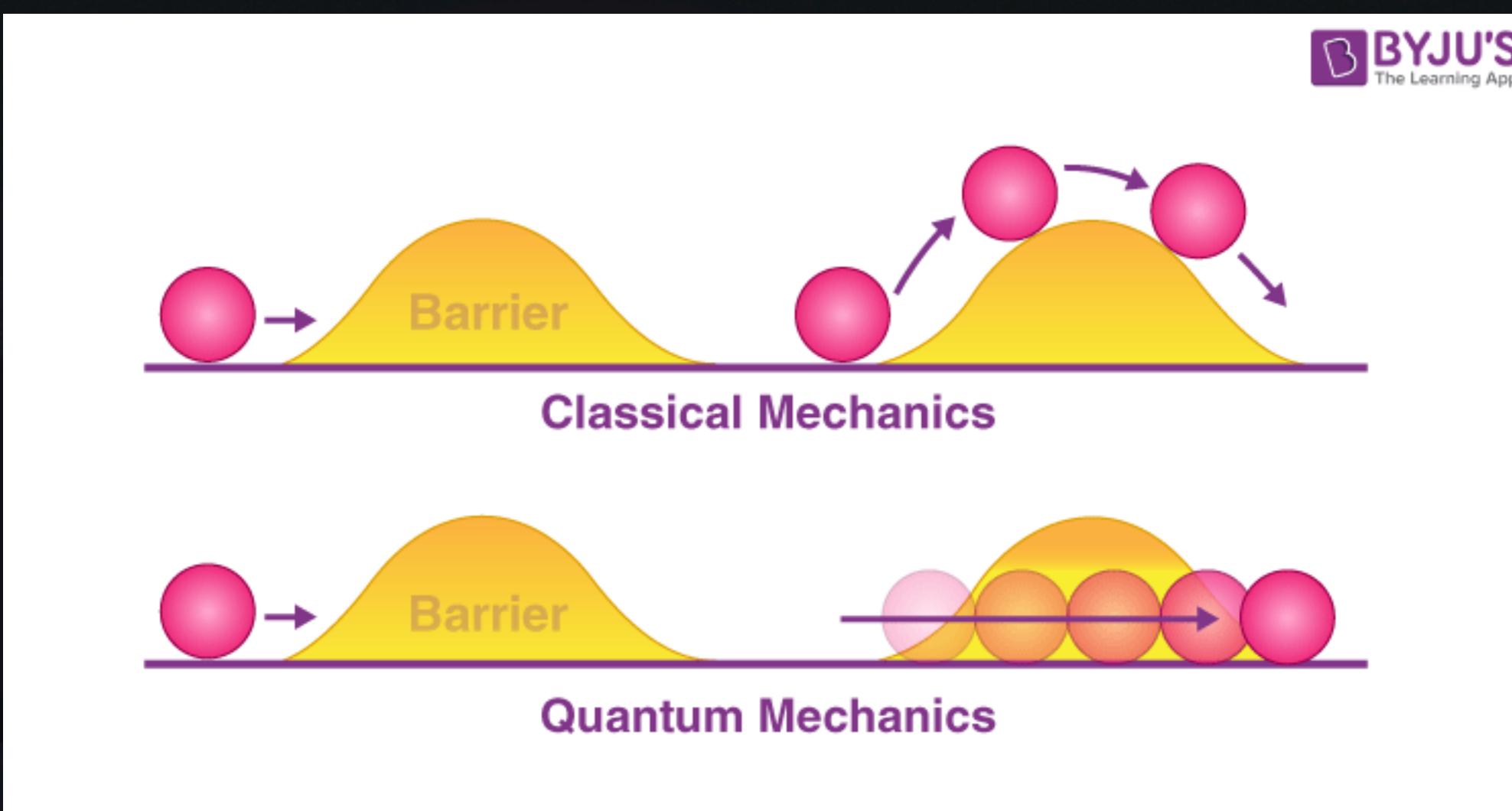
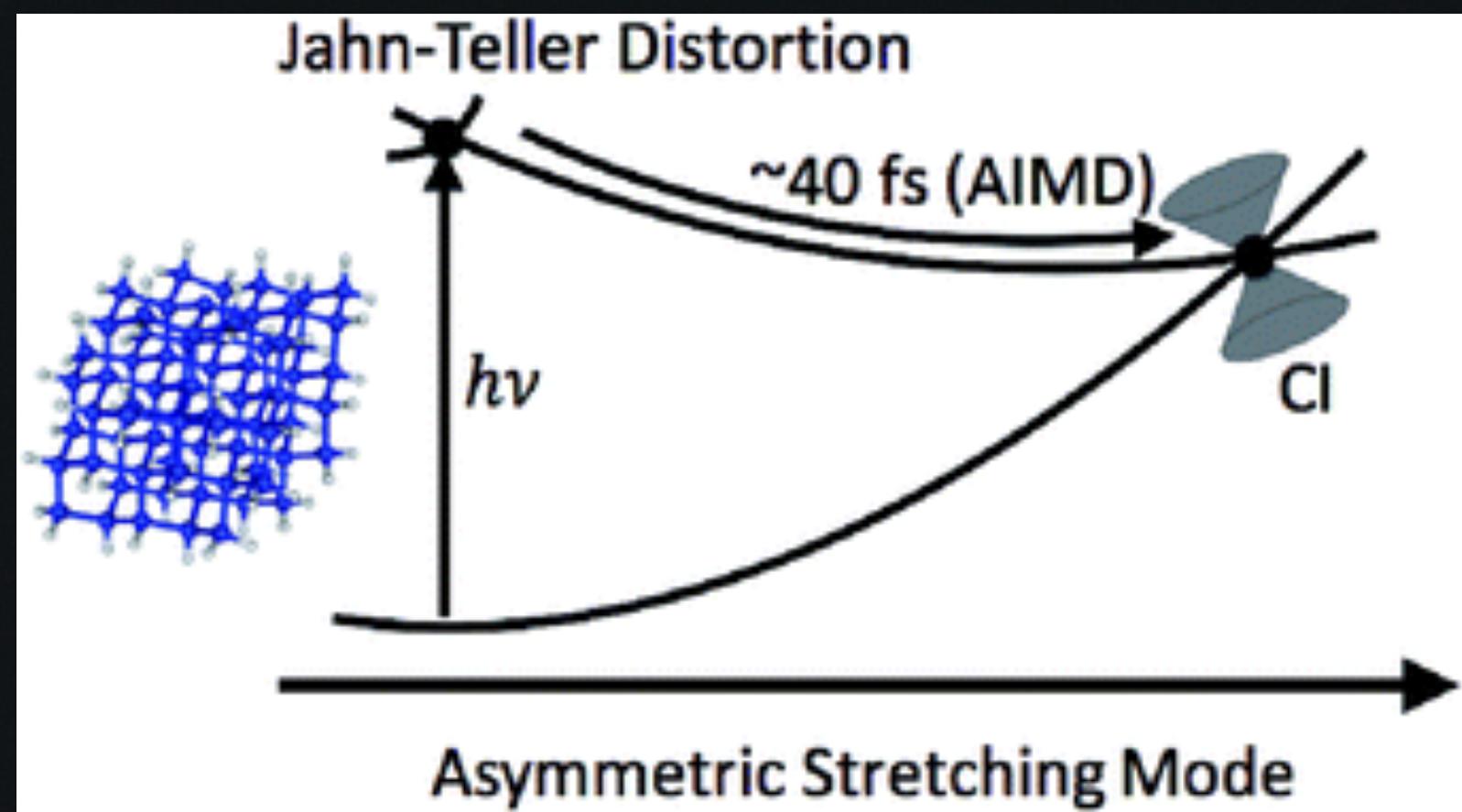
$$\hat{H}_{el}|\Psi_{el}\rangle = E_{el}|\Psi_{el}\rangle \longrightarrow \Psi_{el} = \Psi_{el}(\{\mathbf{r}_i\}, \{\mathbf{R}_{\alpha}\})$$

$$\hat{H}_{Nu}|\Psi_{Nu}\rangle = E_{Nu}|\Psi_{Nu}\rangle$$

$$\hat{H}_{el} = \sum_i^N \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_i^N v(\mathbf{r}_i) + \sum_{i < j}^N \frac{1}{r_{ij}} + \sum_{\alpha < \beta}^N \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}$$

$$\hat{H}_{Nu} = \sum_{\alpha}^N \left( -\frac{1}{2} \nabla_{\alpha}^2 \right) + E_{el}$$

# La Aproximación de Born-Oppenheimer



# Spin-Orbital

$$\hat{H}_{el} = \sum_i^N \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_i^N v(\mathbf{r}_i) + \sum_{i < j}^N \frac{1}{r_{ij}} + \sum_{\alpha < \beta}^N \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$$

$$\langle \alpha | \alpha \rangle = 1 \quad \langle \beta | \beta \rangle = 1$$

$$\begin{array}{c} \psi(\mathbf{r}) \xrightarrow{\hspace{1cm}} \psi(\mathbf{r})\beta(\omega) = \chi(\mathbf{x}) \\ \psi(\mathbf{r}) \xrightarrow{\hspace{1cm}} \psi(\mathbf{r})\alpha(\omega) = \chi(\mathbf{x}) \end{array}$$

# Antisymmetry for fermion



$$\psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = -\psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N)$$

La función de onda no solo debe satisfacer la ecuación de Schrödinger, también debe ser antisimétrica respecto al intercambio virtual.



# Determinante de Slater



$$\langle \mathbf{r}_1\omega_1, \dots, \mathbf{r}_N\omega_N | \Psi_0 \rangle = \Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N}} \det \begin{pmatrix} \chi_1(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{pmatrix}$$

**Notation:**

$$\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle$$

# Pauli exclusion principle



Consideramos un caso simple:

$$\Psi(\mathbf{x}_1 \mathbf{x}_2) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle$$

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\alpha(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(\omega_2)$$

$$\begin{aligned} P(r_1, r_2) dr_1 dr_2 &= \left( \int d\omega_1 d\omega_2 \Psi^* \Psi \right) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \left( |\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2 |\psi_2(\mathbf{r}_1)|^2 \right) \end{aligned}$$

y si  $\psi_1 = \psi_2$ ,

$$P(r_1, r_2) dr_1 dr_2 = |\psi_1(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2 \neq 0$$

# Principio de Exclusión de Pauli



Consideramos otro caso simple:

$$\Psi(\mathbf{x}_1 \mathbf{x}_2) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle$$

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\alpha(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\alpha(\omega_2)$$

$$P(r_1, r_2)dr_1 dr_2 = \left( \int d\omega_1 d\omega_2 \Psi^* \Psi \right) d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{1}{2} \left( |\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2 |\psi_2(\mathbf{r}_1)|^2 - \{ \psi_1^*(\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2) + \psi_1(\mathbf{r}_1)\psi_2^*(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_2) \} \right)$$

y si  $\psi_1 = \psi_2$ ,

$$P(r_1, r_2)dr_1 dr_2 = \frac{1}{2} \left( |\psi_1(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2 |\psi_1(\mathbf{r}_1)|^2 - |\psi_1(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2 - |\psi_1(\mathbf{r}_2)|^2 |\psi_1(\mathbf{r}_1)|^2 \right) = 0$$

# Hartree-Fock

$$E = \langle \Psi | \hat{H} | \Psi \rangle \text{ con } |\Psi\rangle = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle$$



$$E = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | | ij \rangle$$

$$E = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} [ii | jj] - [ij | ji]$$

$$f(i)\chi(\mathbf{x}_i) = \epsilon_i\chi(\mathbf{x}_i)$$



$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1} z_{\alpha} \frac{z_{\alpha}}{r_{i\alpha}} + V(i)^{HF} \quad \} \text{ Fock operator}$$

Fock, V.: (1930) Z. Phys. 61, 126-148.

Slater, J.C.: Phys . Rev. 35, 210-211 (1930).

# Hartree-Fock - Fock operator

$$f(i)\chi(\mathbf{x}_i) = \epsilon_i\chi(\mathbf{x}_i)$$

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1} z_\alpha r_{i\alpha} + V(i)^{HF}$$

$$f(i) = h(i) + \sum_j J_j - K_j$$

$$\rightarrow f(1)\chi_a(1) = \left[ h(1) + \sum_b \int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_b(2) \right] \chi_a(1)$$

# Hartree-Fock - Roothaan-Hall equations

Closed-shell Hartree-Fock:

$$\chi_i(\mathbf{x}) = \begin{cases} \psi_i(\mathbf{r})\alpha(\omega) \\ \psi_i(\mathbf{r})\beta(\omega) \end{cases}$$

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle = |\psi_1(\mathbf{x}_1)\bar{\psi}_1(\mathbf{x}_2)\cdots\psi_{N/2}(\mathbf{x}_N)\bar{\psi}_{N/2}(\mathbf{x}_N)\rangle$$

$$f(1)\psi_i(\mathbf{r}_1) = \epsilon_i\psi_i(\mathbf{r}_1)$$

$$f(1) = 2h(1) + \sum_i^{N/2} 2J_i(1) - K_i(1)$$

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu} \quad i = 1, 2, \dots, K$$

# Hartree-Fock - Roothaan-Hall equations

$$\psi_1 = c_{11}\phi_1 + c_{21}\phi_2$$

$$\psi_2 = c_{12}\phi_1 + c_{22}\phi_2$$

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu} \quad i = 1, 2, \dots, K$$

$$\hat{F}(c_{11}\phi_1 + c_{21}\phi_2) = \varepsilon_1(c_{11}\phi_1 + c_{21}\phi_2)$$

$$\hat{F}(c_{12}\phi_1 + c_{22}\phi_2) = \varepsilon_2(c_{12}\phi_1 + c_{22}\phi_2)$$

$$c_{11}\langle\phi_1 | \hat{F} | \phi_1\rangle + c_{21}\langle\phi_1 | \hat{F} | \phi_2\rangle = \varepsilon_1(c_{11}\langle\phi_1 | \phi_1\rangle + c_{21}\langle\phi_1 | \phi_2\rangle)$$

$$c_{11}\langle\phi_2 | \hat{F} | \phi_1\rangle + c_{21}\langle\phi_2 | \hat{F} | \phi_2\rangle = \varepsilon_1(c_{11}\langle\phi_2 | \phi_1\rangle + c_{21}\langle\phi_2 | \phi_2\rangle)$$

$$c_{12}\langle\phi_1 | \hat{F} | \phi_1\rangle + c_{22}\langle\phi_1 | \hat{F} | \phi_2\rangle = \varepsilon_2(c_{12}\langle\phi_1 | \phi_1\rangle + c_{22}\langle\phi_1 | \phi_2\rangle)$$

$$c_{12}\langle\phi_2 | \hat{F} | \phi_1\rangle + c_{22}\langle\phi_2 | \hat{F} | \phi_2\rangle = \varepsilon_2(c_{12}\langle\phi_2 | \phi_1\rangle + c_{22}\langle\phi_2 | \phi_2\rangle)$$

$$c_{11}F_{11} + c_{21}F_{12} = \varepsilon_1(c_{11}S_{11} + c_{21}S_{12})$$

$$c_{11}F_{21} + c_{21}F_{22} = \varepsilon_1(c_{11}S_{21} + c_{21}S_{22})$$

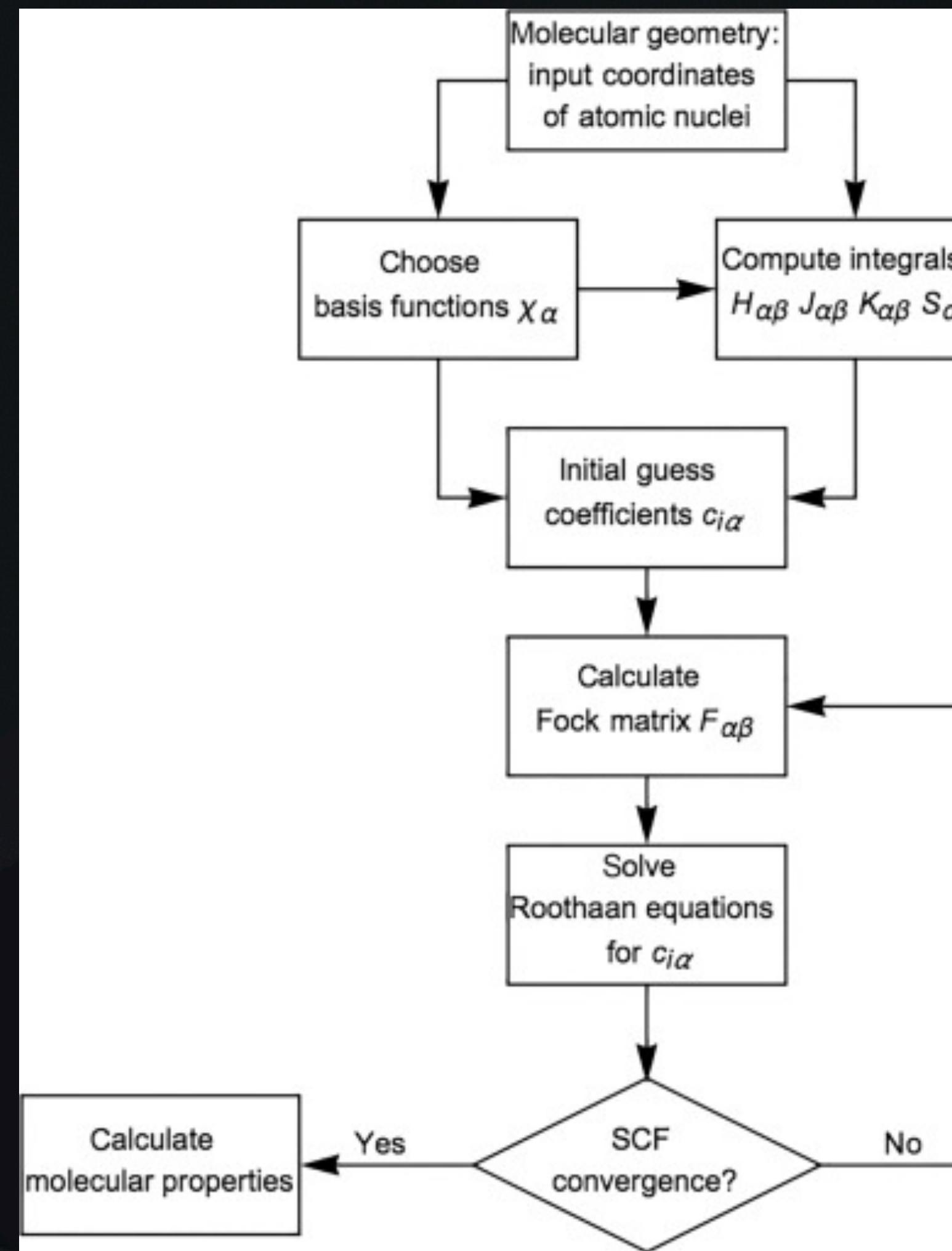
$$c_{12}F_{11} + c_{22}F_{12} = \varepsilon_2(c_{12}S_{11} + c_{22}S_{12})$$

$$c_{12}F_{21} + c_{22}F_{22} = \varepsilon_2(c_{12}S_{21} + c_{22}S_{22})$$

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \begin{pmatrix} \varepsilon_{11} & 0 \\ 0 & \varepsilon_{22} \end{pmatrix}$$

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

# SCF Method

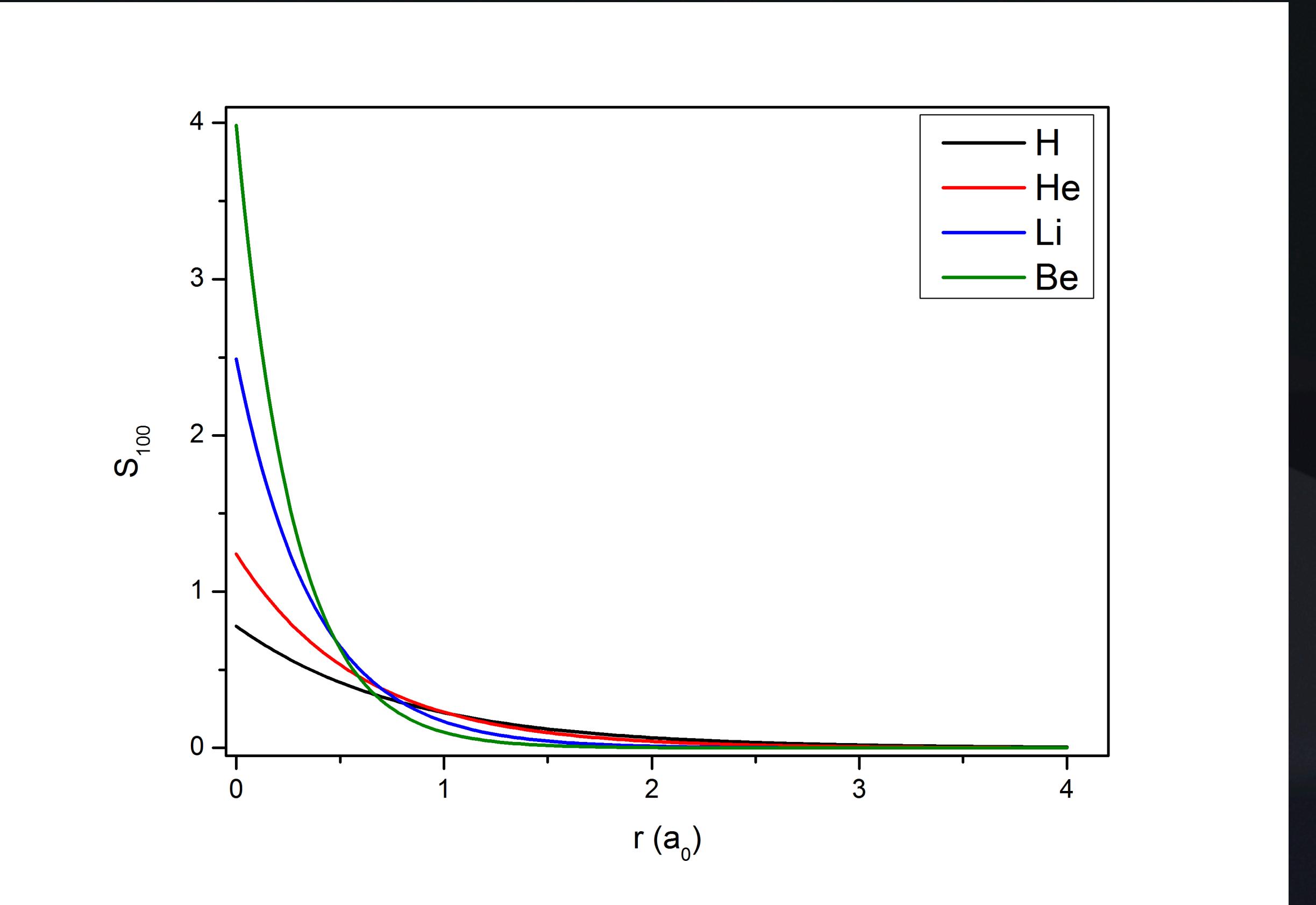
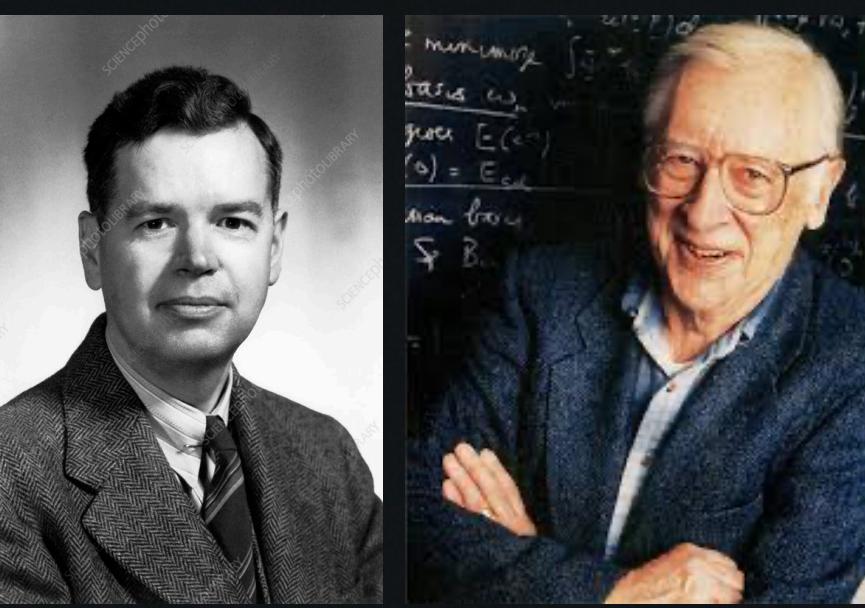


# Basis-Set

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu} \quad i = 1, 2, \dots, K$$

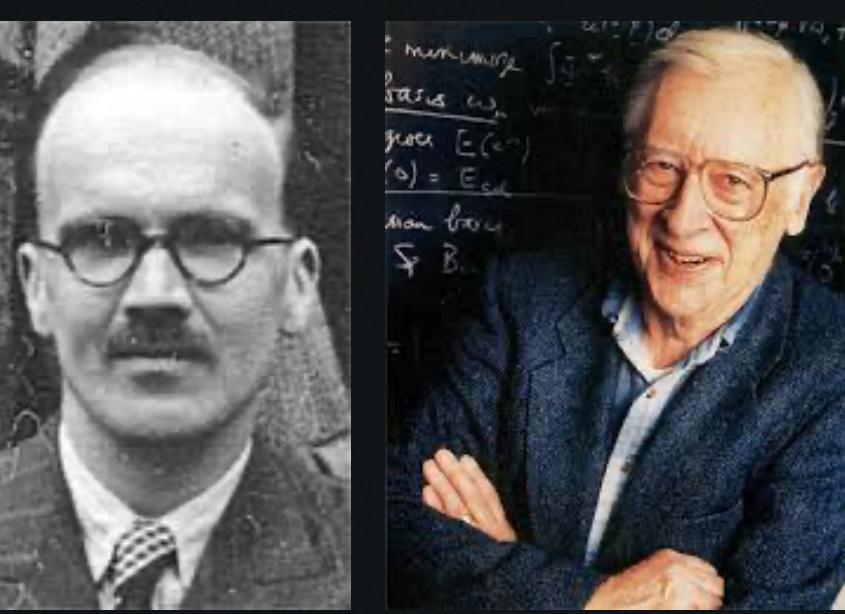
Slater type atomic orbitals (STOs)

$$S_{nlm}(r, \theta, \phi) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi)$$

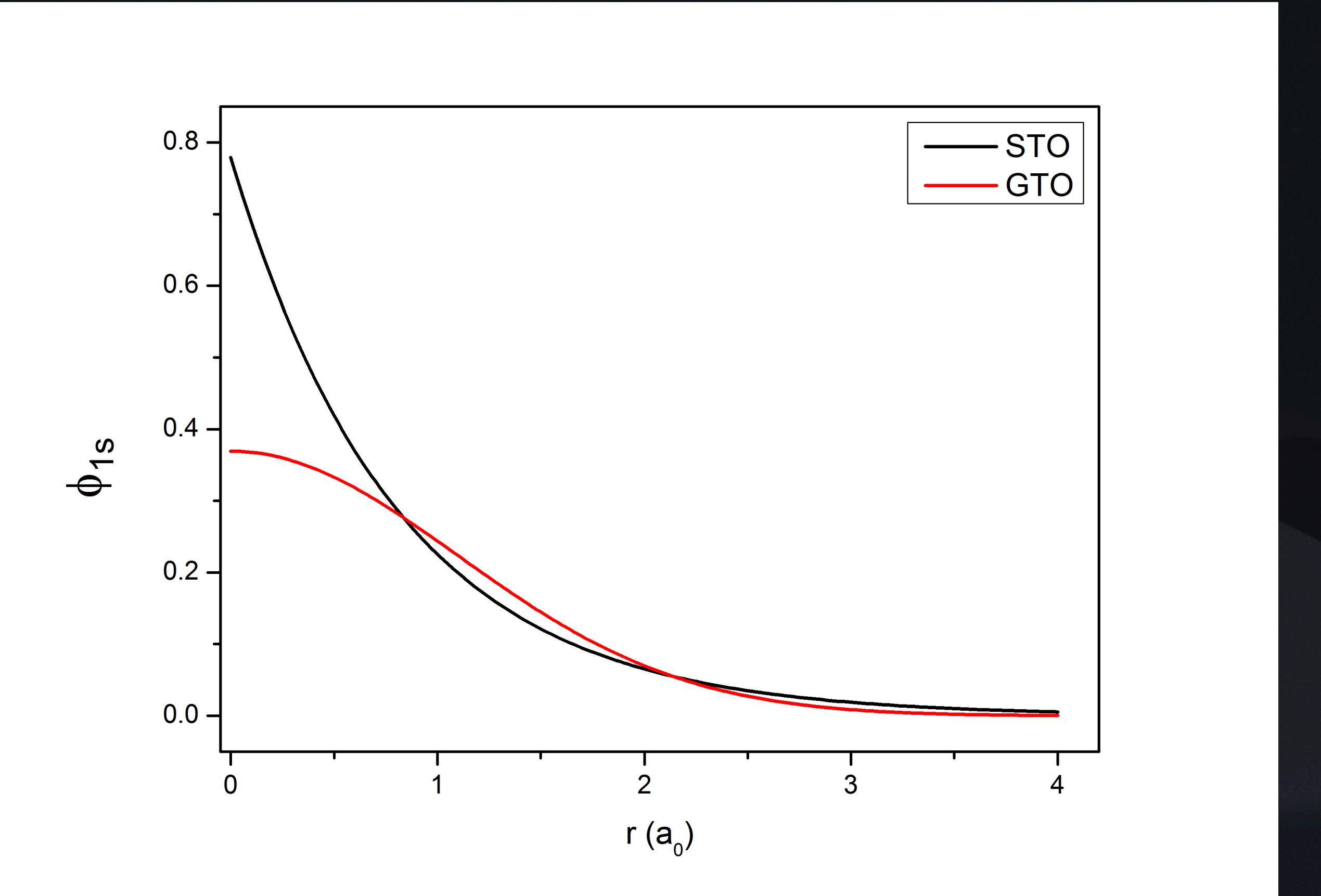


# Basis-Set

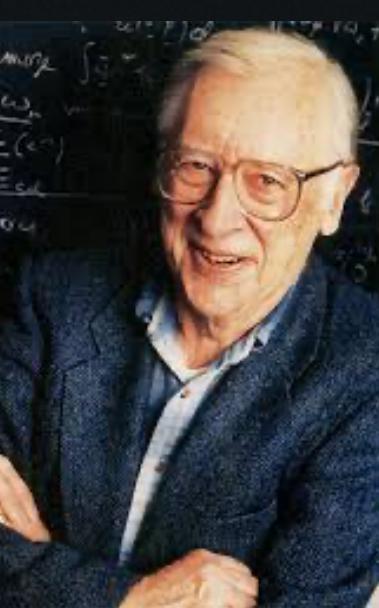
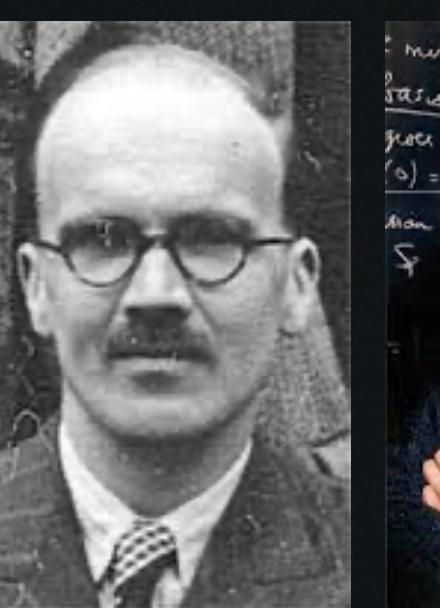
Gaussian type atomic orbitals (GTOs)



$$G_{nlm}(r, \theta, \phi) = N_n r^{n-1} e^{-\alpha r^2} Y_l^m(\theta, \phi)$$



# Basis-Set



Why do we use GTOs?

$$G_{nlm}(\mathbf{r} - \mathbf{R}, \theta, \phi) = N_n r^{n-1} e^{-\alpha|\mathbf{r}-\mathbf{R}|^2} Y_l^m(\theta, \phi)$$

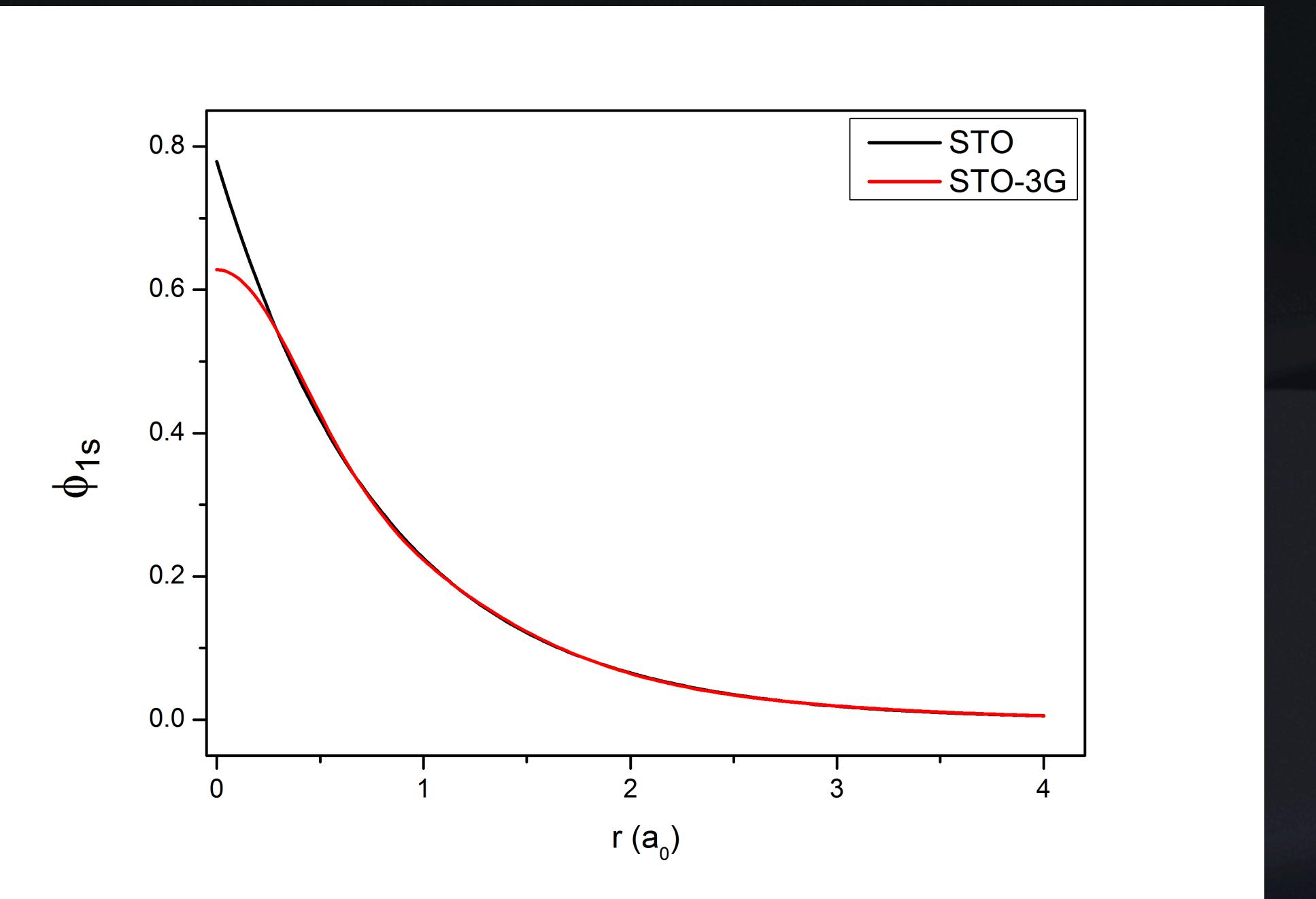
$$e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} e^{-\beta|\mathbf{r}-\mathbf{R}_B|^2} \longrightarrow e^k e^{-\Gamma|\mathbf{r}-\mathbf{R}_p|^2}$$

# Basis-Set

$$G_{nlm}(\mathbf{r} - \mathbf{R}, \theta, \phi) = N_n r^{n-1} e^{-\alpha |\mathbf{r} - \mathbf{R}|^2} Y_l^m(\theta, \phi)$$



$$\begin{aligned}\phi_{1s}^{STO}(r, 1.24) &= \sum_{i=1}^3 d_{1s_i} \phi_{1s}^{GTO}(r, \alpha_{1s_i}) \\ &= 0.4446 \phi_{1s}^{GTO}(r, 0.1688) + 0.5353 \phi_{1s}^{GTO}(r, 0.6239) + 0.1543 \phi_{1s}^{GTO}(r, 3.425)\end{aligned}$$



Boys, S. F., 1950, Proc. R. Soc. London, Ser. A 200, 542.

Pople, J. A.; Hehre, W. J. (1978). "Computation of electron repulsion integrals involving contracted Gaussian basis functions". *J. Comput. Phys.* **27** (2): 161–168.

# Basis-Set -> Families



- Slater types orbitals (STOs)
- Gaussian type orbitals (GTOs) -> Pople
- Dunning's Correlation-Consistent Basis Sets
- Effective core potential (ECP) -> LanL2DZ and Stuttgart-ECP

Boys, S. F., 1950, Proc. R. Soc. London, Ser. A 200, 542.

Pople, J. A.; Hehre, W. J. (1978). "Computation of electron repulsion integrals involving contracted Gaussian basis functions". *J. Comput. Phys.* **27** (2): 161–168.

Dunning T. H.; "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen". *J. Chem. Phys.* 15 January 1989; 90 (2): 1007–1023.

P. Fuentealba, H. Preuss, H. Stoll, L. v. Szenthelyi, *Chem. Phys. Lett.* 89, 418 (1982).

# Gaussian70 -> 16

## Gaussian 70

Program Title: GAUSSIAN 70: Ab Initio SCF-MO Calculations on Organic Molecules

Author: W. J. Hehre  
University of California, Irvine

W. A. Lathan  
University of Rochester

R. Ditchfield  
Dartmouth College

M. D. Newton  
Brookhaven National Laboratory

J. A. Pople  
Carnegie Mellon University

Lines of Code: 13370

Platform/Language: FORTRAN IV (IBM 360/370)

Recommended Citation: W. J. Hehre, J. A. Pople et al., QCPE, 1, 236 (1973)

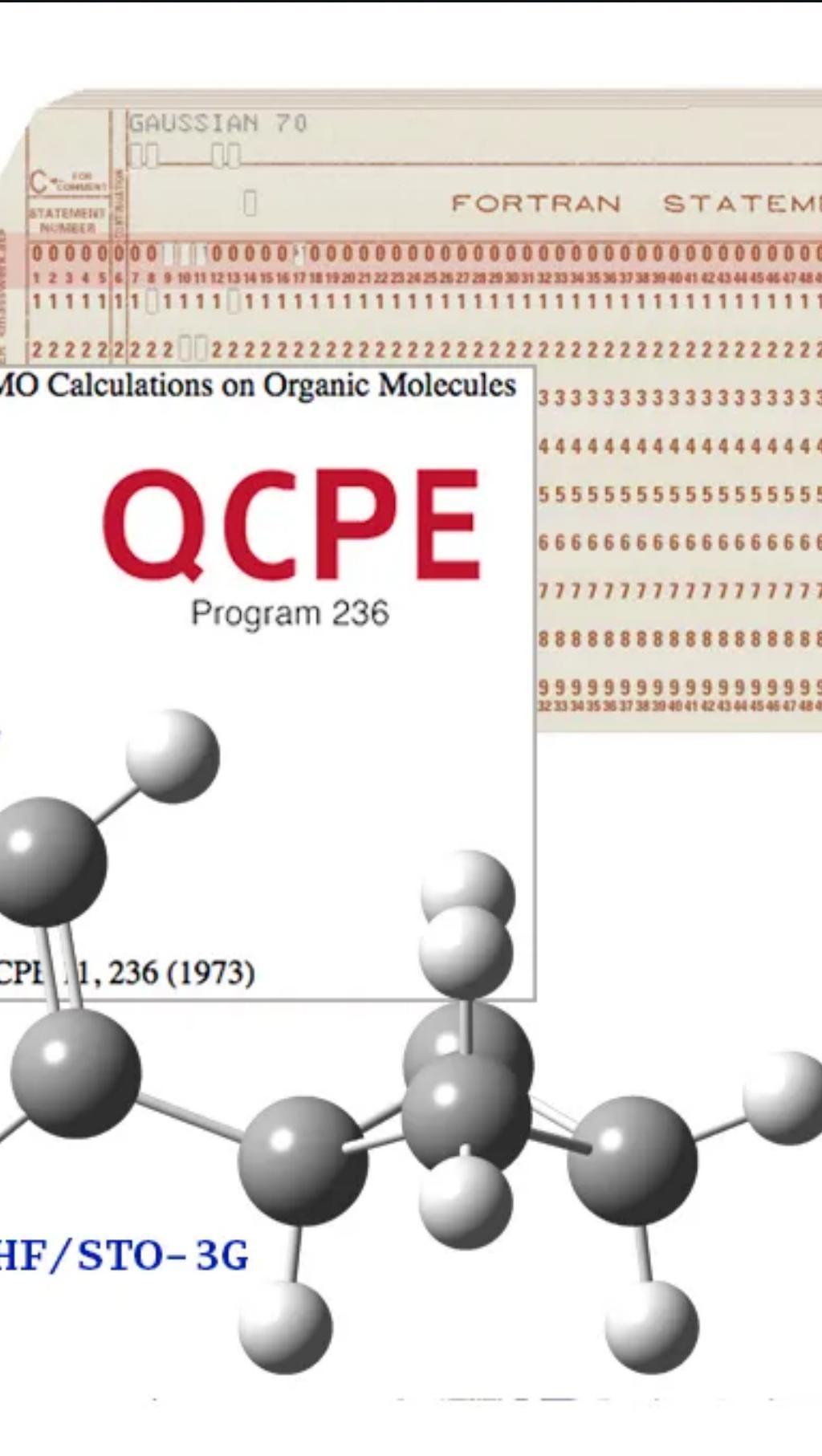
Major Features:

- Hartree-Fock energies
- Basis sets with s and p functions
- Dipole moments

Challenging Calculation:

- Vinylcyclobutane HF/STO-3G energy

QCPE Program 236



The screenshot shows the Gaussian 70 software interface. On the left, there is a molecular model of vinylcyclobutane. To the right of the model is a large block of FORTRAN code, which is a listing of the program's source code. The code is organized into sections labeled 'FORTRAN STATEMENT' and 'STATEMENT NUMBER'. The entire interface has a light beige background.

## Gaussian 16

Major New Features:

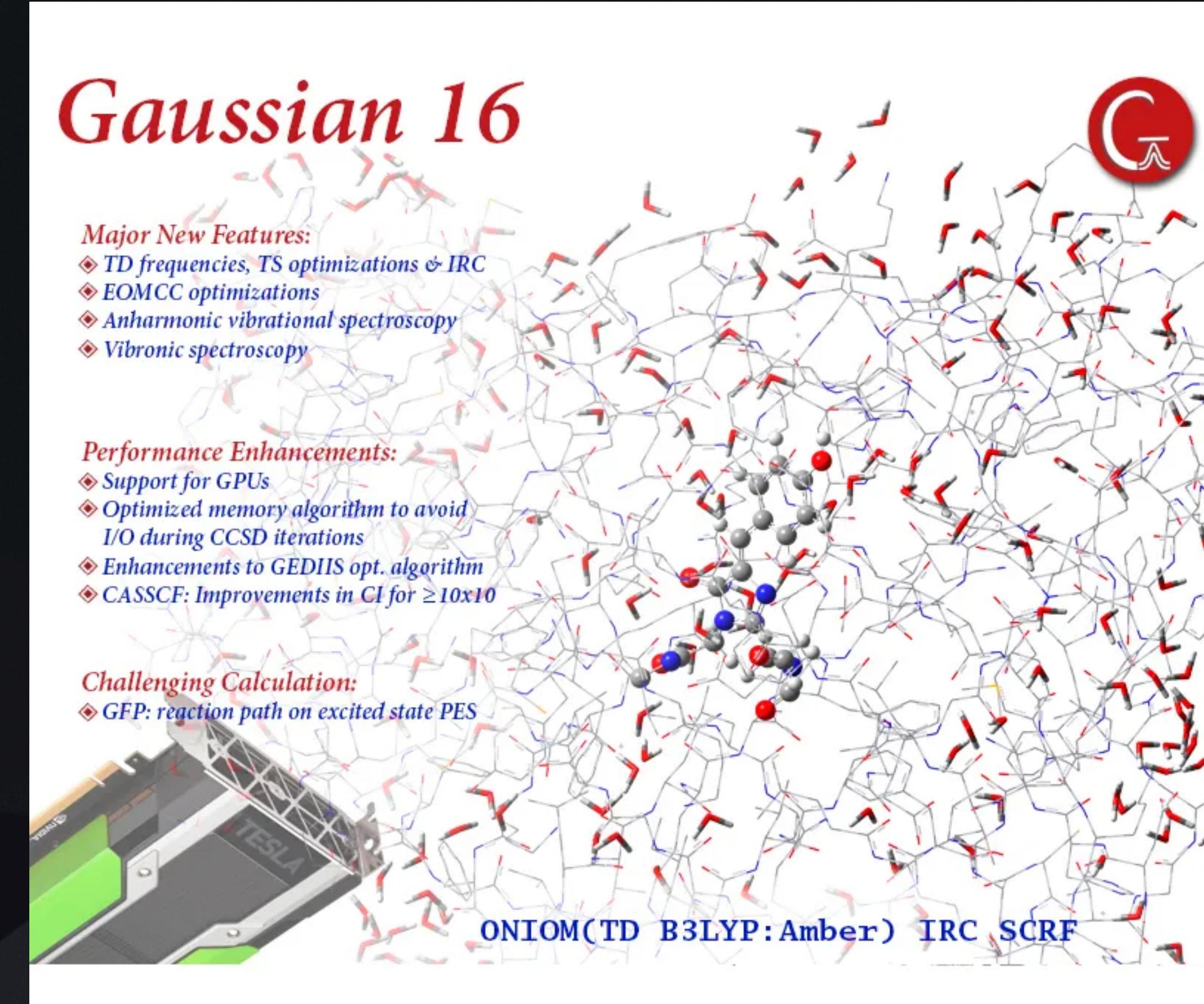
- TD frequencies, TS optimizations & IRC
- EOMCC optimizations
- Anharmonic vibrational spectroscopy
- Vibronic spectroscopy

Performance Enhancements:

- Support for GPUs
- Optimized memory algorithm to avoid I/O during CCSD iterations
- Enhancements to GEDIIS opt. algorithm
- CASSCF: Improvements in CI for  $\geq 10 \times 10$

Challenging Calculation:

- GFP: reaction path on excited state PES



The screenshot shows the Gaussian 16 software interface. It features a complex molecular system with many atoms and bonds, some of which are highlighted in red and blue. Arrows indicate electron flow or movement within the molecule. In the bottom left corner, there is a photograph of a Tesla GPU card. The overall background is white with a red circular logo containing a stylized letter 'G' in the top right corner.

# El Premio nobel en ... Química.



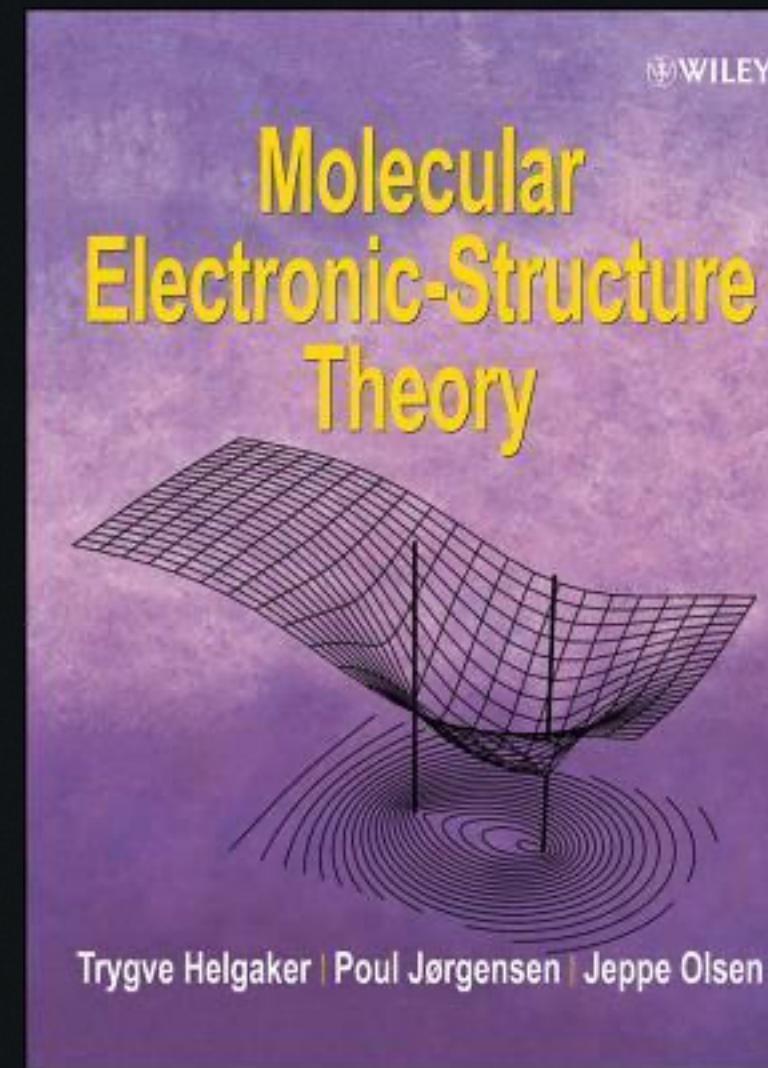
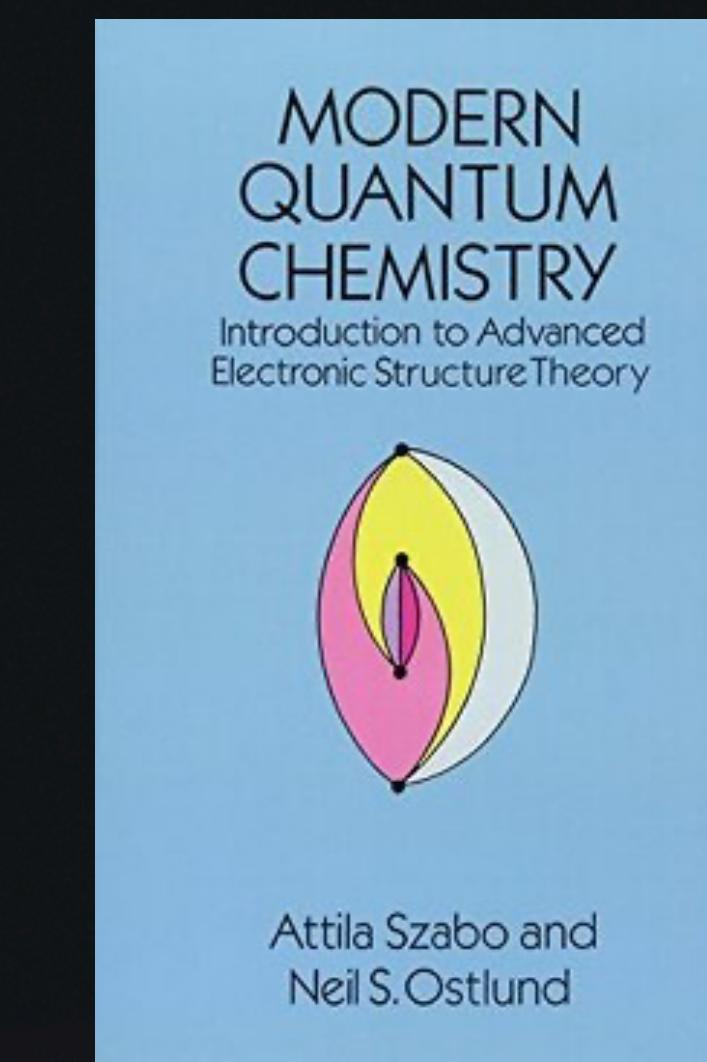
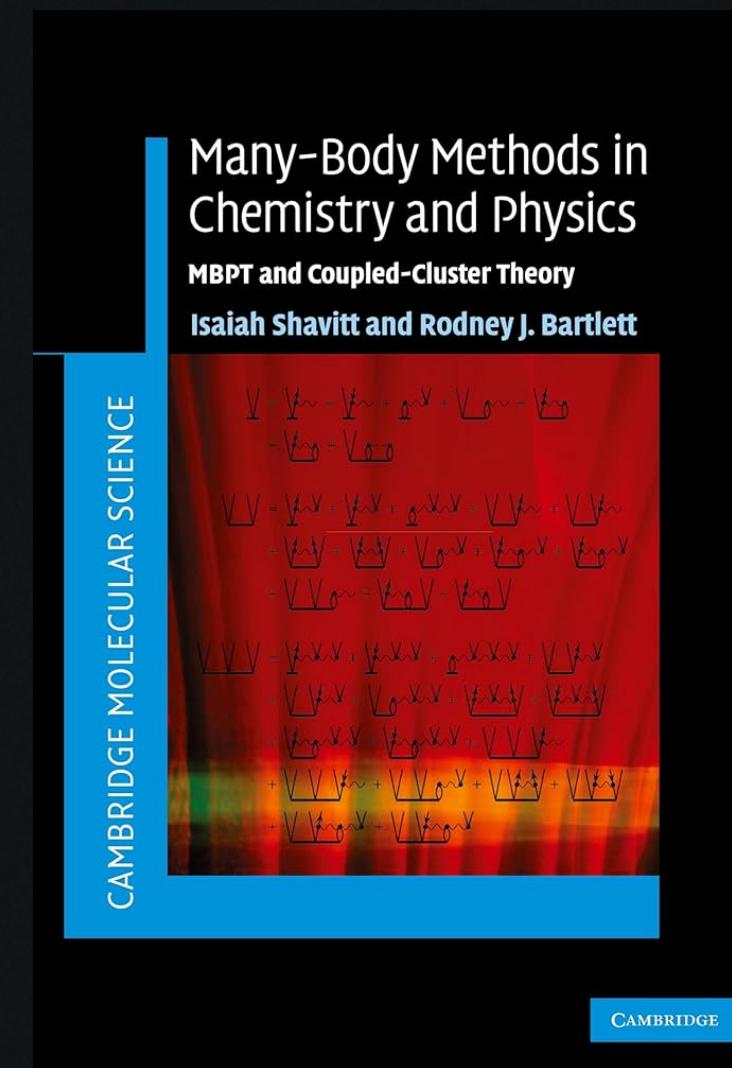
Prof. John Pople and King Carl XVI Gustaf.



Sir John Pople and Queen Elizabeth.

*"for his development of computational methods in quantum chemistry"*

# Books



# Hartree-Fock

Manos a la obra

$$f(1)\chi_a(1) = \left[ h(1) + \sum_b \int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} (1 - \mathcal{P}_{12}) \chi_b(2) \right] \chi_a(1)$$

- git clone [https://github.com/simmat-uchile/MiniSchool\\_SimMat\\_2025.git](https://github.com/simmat-uchile/MiniSchool_SimMat_2025.git)

# Density-Functional Theory

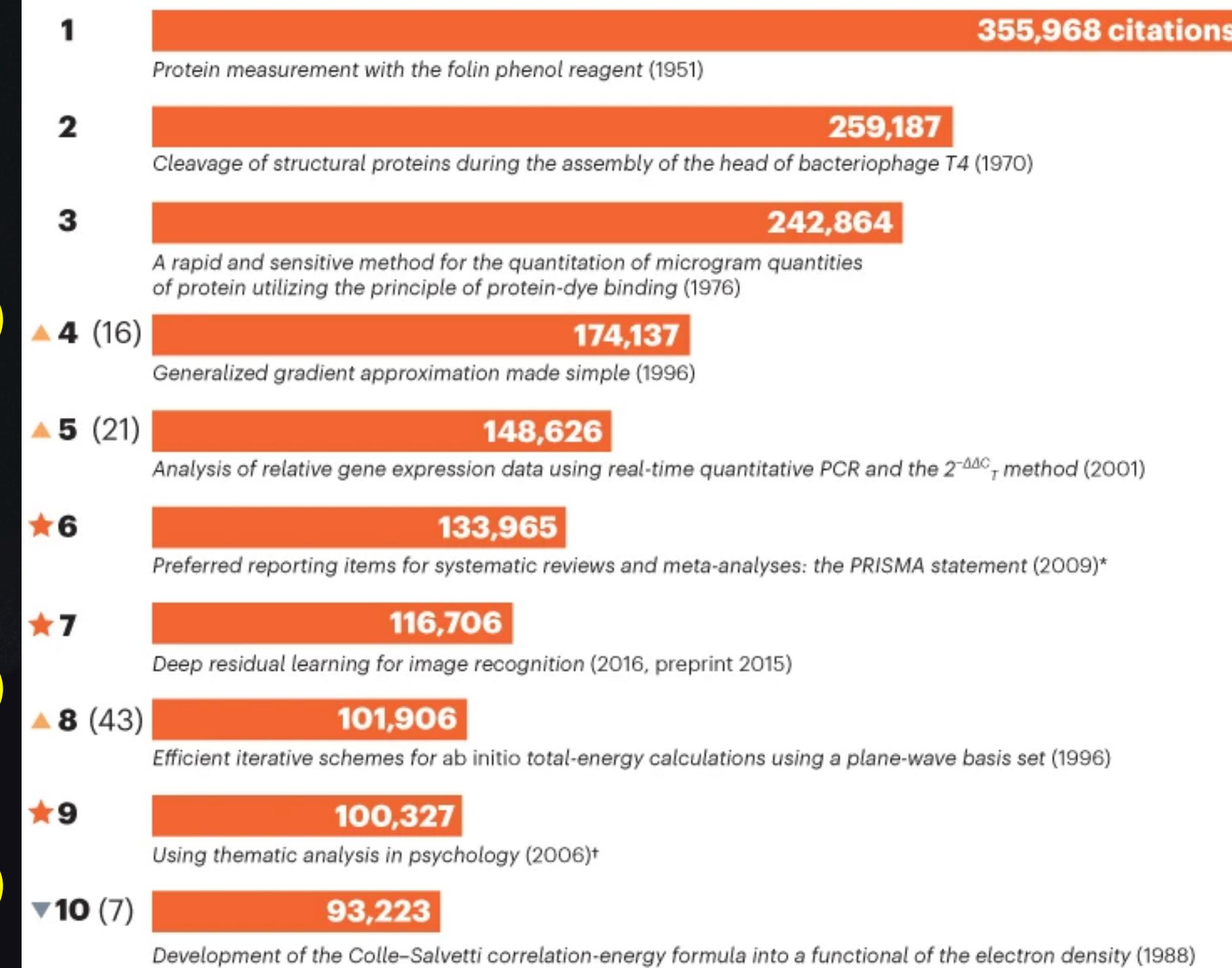
## Una pequeña Introducción

$$\frac{\delta}{\delta\rho}\left(E_v[\rho] - \mu\left(\int d\mathbf{r} \rho(\mathbf{r}) - N\right)\right) = 0$$

# Impacto de la DFT

## TOP TEN CITED PAPERS

Just 3 papers have more than 200,000 citations each, according to the Web of Science database. All three cover biological laboratory techniques. This update to a 2014 list of most-cited articles shows that the top three papers remain unchanged. But there have been shifts in the positions of others (triangles), and some additions that were not on the previous list (orange stars). For alternative rankings from two other databases, and a median ranking across all three, see Supplementary information ([go.nature.com/425g9dn](http://go.nature.com/425g9dn)).



Data show citations from Web of Science 'Core Collection' journals as of March 2025, to permit comparison with 2014 list (*Nature* **514**, 550–553; 2014). Orders would change if citation metrics from other databases were included (see Supplementary information).

\*Paper was published in multiple journals simultaneously. This total aggregates citations to all journal versions.

†Corrected for data error in Web of Science, which lists a different paper by the same authors.

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# El Premio nobel en ... Química.

“However, because of my now German nationality, I was not allowed into the chemistry building, where war work was in progress, and hence I could not enroll in any chemistry courses. (In fact, the last time I attended a chemistry class was in my English school at the age of 17.) Since chemistry was required, this seemed to sink any hope of enrolling..”



*“for his development of the density-functional theory”*

# Densidad Electrónica I

$$\rho(\mathbf{r}) = N \sum_s \int \Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) \Psi^*(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

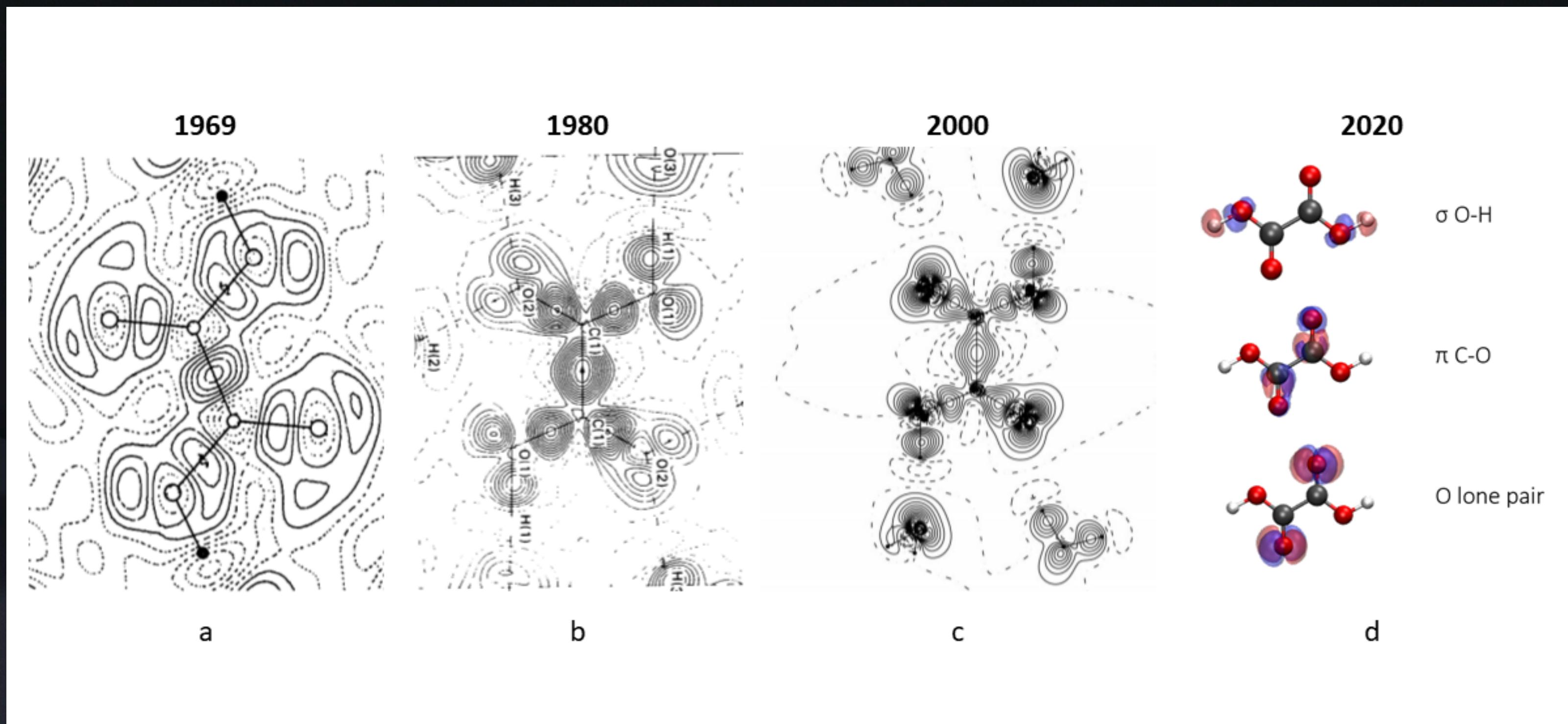
$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho} | \Psi \rangle \equiv = \left\langle \Psi \left| \sum_i^N \delta^3(\mathbf{r} - \mathbf{r}_i) \right| \Psi \right\rangle$$

$$\int d\mathbf{r} \rho(\mathbf{r}) = N$$

La densidad electrónica es el número medio de electrones por unidad de volumen.

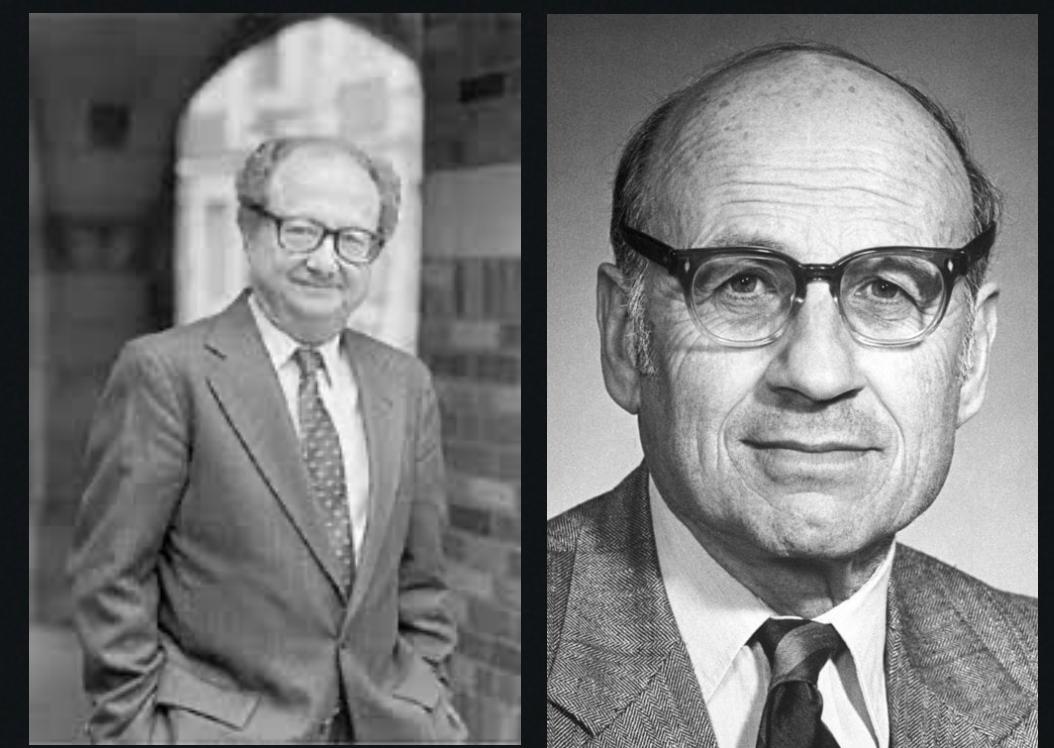
# Densidad Electrónica III

- Es un observable y en la práctica es accesible experimentalmente -> Cristalografía electrónica y cristalográfica cuántica.
- Es una función de 3 variables.



# Preludio de Hohenberg-Kohn I

Nuestro problema es un conjunto de N electrones interactuantes, cuyo Hamiltoniano viene dado por:



$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \frac{1}{2} \sum_{i,j}^N \frac{1}{r_{i,j}} + \hat{V}_{ex}$$

—————>  $\hat{V}_{ex} = - \sum_{\alpha,i} \frac{Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}_i|} = \sum_i v_{ext}(\mathbf{r}_i)$

¿En qué se diferencian el Hamiltoniano átomo de níquel y el ciclobutadieno?

Solo en el potencial externo!

$$\hat{H}_{Ni} = -\frac{1}{2} \sum_i^{28} \nabla_i^2 + \frac{1}{2} \sum_{i,j}^{28} \frac{1}{r_{i,j}} + \hat{V}_{ex,Ni}$$
$$\hat{H}_{cb} = -\frac{1}{2} \sum_i^{28} \nabla_i^2 + \frac{1}{2} \sum_{i,j}^{28} \frac{1}{r_{i,j}} + \hat{V}_{ex,cb}$$

En este punto ya es medio obvio que  $\hat{V}_{ext} \rightarrow \Psi$ , pero es la relación invertible?

# Preludio de Hohenberg-Kohn II

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{ext})\Psi = E\Psi$$

y,

$$(\hat{T} + \hat{V}_{ee} + \hat{V}'_{ext})\Psi = E'\Psi$$

Si restamos,

$$(\hat{V}_{ext} - \hat{V}'_{ext})\Psi = (E - E')\Psi$$

$$\hat{V}_{ext} - \hat{V}'_{ext} = E - E'$$

lo que es claramente falso, ya que los potenciales difieren por más que una constante aditiva.

Así,  $\Psi \leftrightarrow \hat{V}_{ext}$ .

Por otro lado, como  $\Psi$  determina  $\rho(\mathbf{r})$  entonces,  $\hat{V}_{ext}$  determina  $\rho(\mathbf{r})$ . Lo que demuestra el primer teorema de Hohenberg-Kohn es que relación también es invertible, es decir,  $\rho(\mathbf{r})$  determina  $\hat{V}_{ext}$ . La demostración también es por contradicción.

# First Theorem of Hohenberg-Kohn

The first theorem states that for a system of  $N$  interacting electrons in an external potential  $v_{ext}(\mathbf{r})$ , there is a one-to-one correspondence, up to a constant, between said external potential, the non-degenerate ground-state wavefunction  $\Psi_0$  resulting from the solution of the Schrödinger equation and its associated ground-state density  $\rho$ ,

$$v_{ext}(\mathbf{r}) \iff |\Psi_0\rangle \iff \rho(\mathbf{r}) = N \sum_{\sigma_1 \dots \sigma_N} \int d\mathbf{r}_2 \dots \mathbf{r}_N |(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N) |\Psi_0\rangle|^2$$

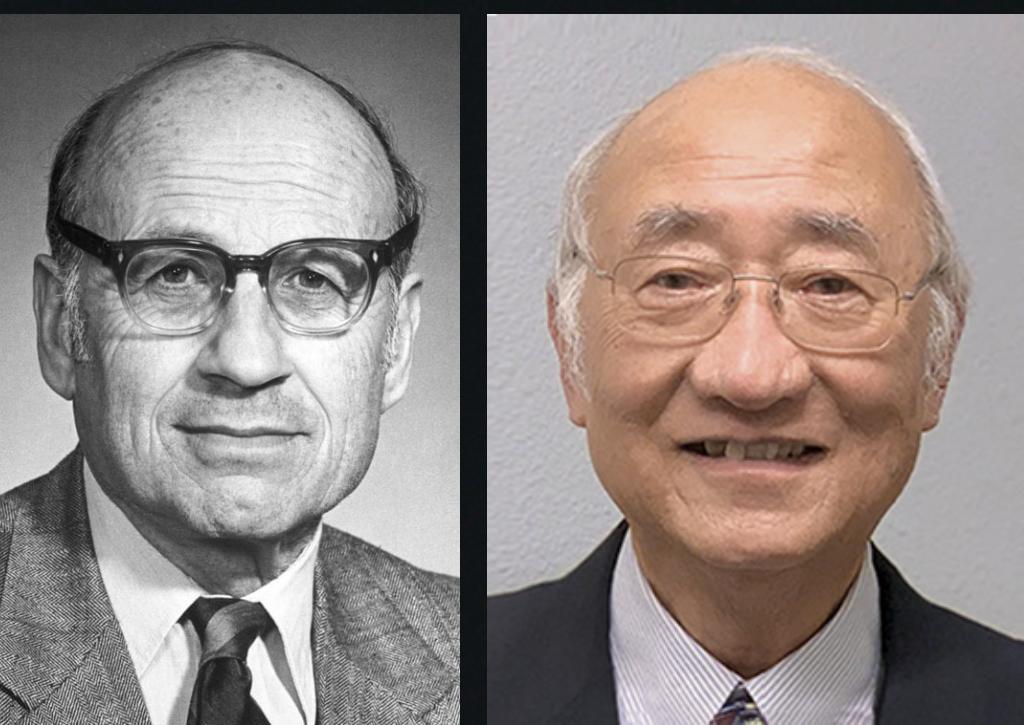
unique (up to some additive constant in  $v_{ext}$ )

# Second Theorem of Hohenberg-Kohn

The second Hohenberg-Kohn theorem states the existence of a variational principle for  $E_v[\rho]$ . This is, for a trial density  $\tilde{\rho}(\mathbf{r})$ , such that  $\tilde{\rho}(\mathbf{r}) \geq 0$  and  $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$ ,

$$E_v[\rho] \leq E_v[\tilde{\rho}]$$

# Kohn-Sham Method



$$E_v[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r}$$

$$E_v[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r}$$

$$F[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})]$$

$$E_{xc}[\rho(\mathbf{r})] \equiv T[\rho(\mathbf{r})] - T_s[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] - J[\rho(\mathbf{r})]$$

$$\mu = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_{KS}(\mathbf{r})$$

$$v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

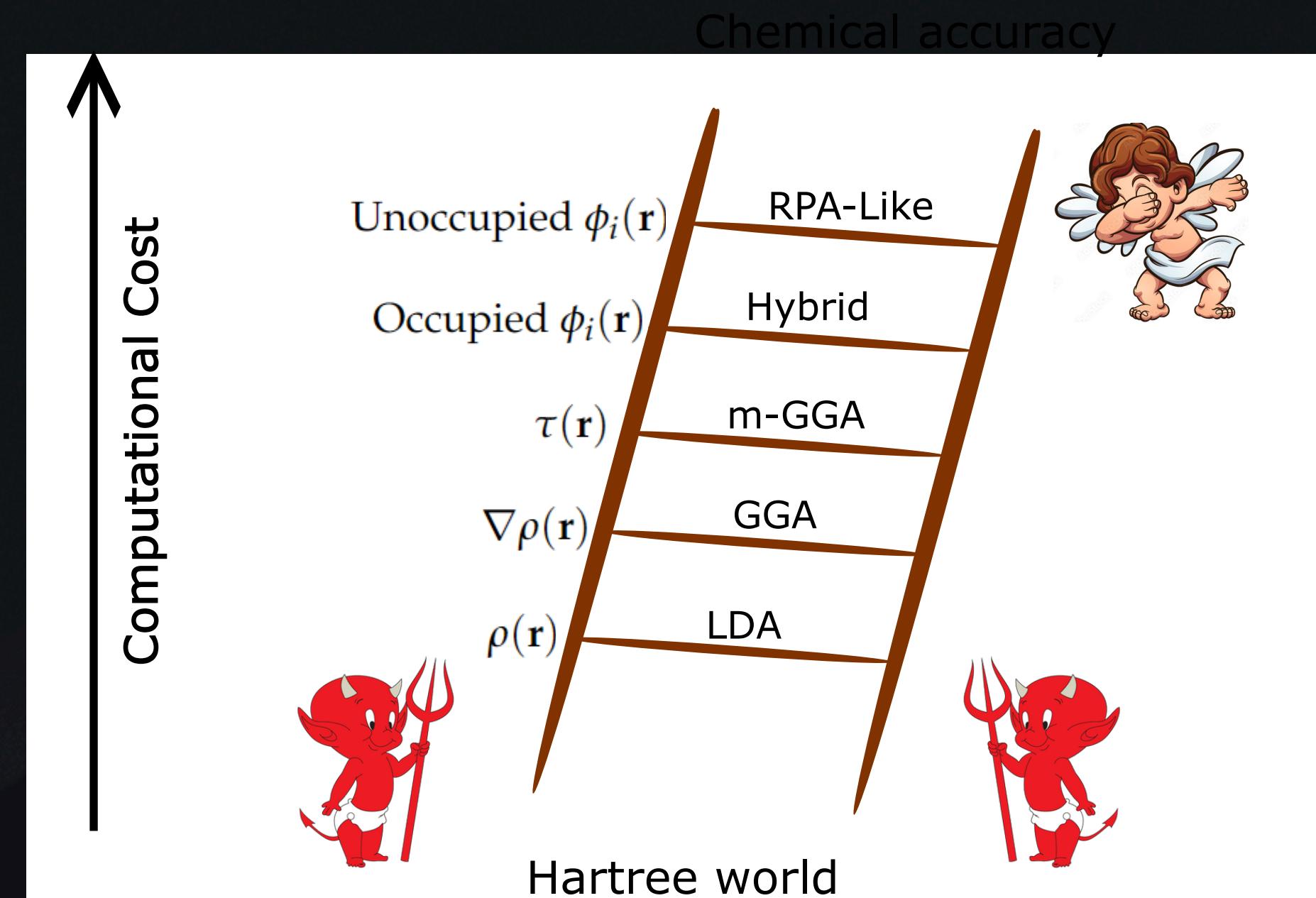
$$= v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}; \rho(\mathbf{r}))$$

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] + \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

# Functionals - Zoo



# LDA-LSDA

$$E_{xc}^{LDA} \equiv \int e_{xc}(\rho) \rho(\mathbf{r}) d\mathbf{r}$$

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

The diagram illustrates the decomposition of the exchange-correlation energy. It starts with the total exchange-correlation energy  $E_{xc}[\rho]$  at the top left. A horizontal arrow points from this expression to the sum of the exchange energy  $E_x[\rho]$  and the correlation energy  $E_c[\rho]$ . From each of these two terms, a curved arrow points down to their respective LDA components:  $e_x(\rho) = -C_x \rho^{1/3}(\mathbf{r})$  and  $e_C(\rho) \approx e_C(\rho)^{VWN}$ .

$$e_x(\rho) = -C_x \rho^{1/3}(\mathbf{r})$$
$$e_C(\rho) \approx e_C(\rho)^{VWN}$$