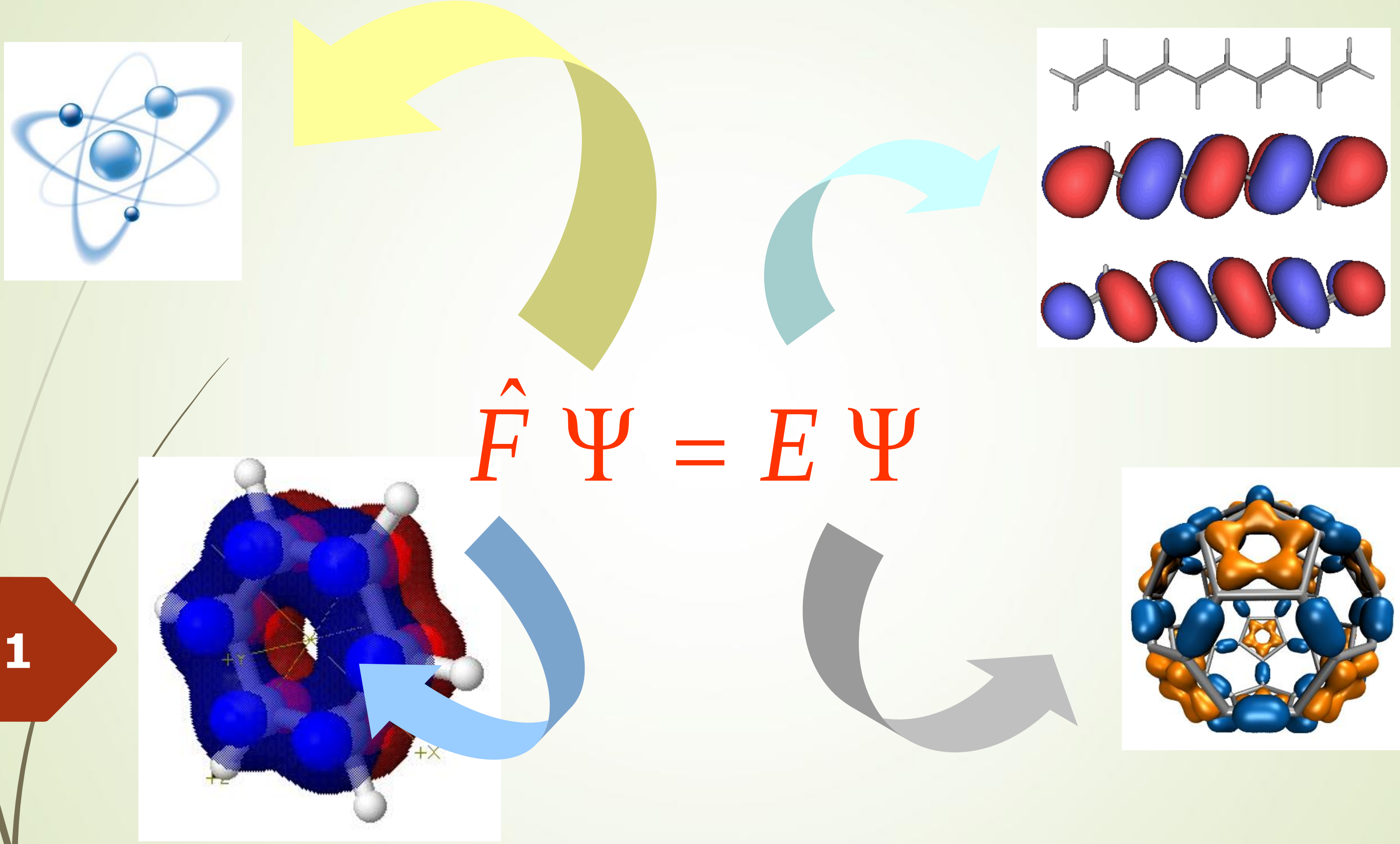
Self-Consistent Field (SCF)



$$\hat{F}\,\Psi = E\,\Psi$$

سید محمد اعظمی

بهمن ۱۴۰۲

Time-independent Schrödinger equation

$$\hat{H}\,\Psi = E\,\Psi$$

Electron-nuclear attraction

$$\hat{H} = -\tfrac{1}{2}\sum_{i}\nabla_{i}^{2} - \sum_{i} r_{i}^{-1} + \boxed{\sum_{ij} r_{ij}^{-1}}$$

Kinetic energy

Electron-electron repulsion

Responsible for electronic correlation !

Schrödinger equation: Is that ALL ?

No !!!

Boundary conditions limit the solutions.

Electrons are Fermions!

Determinantal wave function

$$\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N) \end{vmatrix}$$

Slater determinant

He atom

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

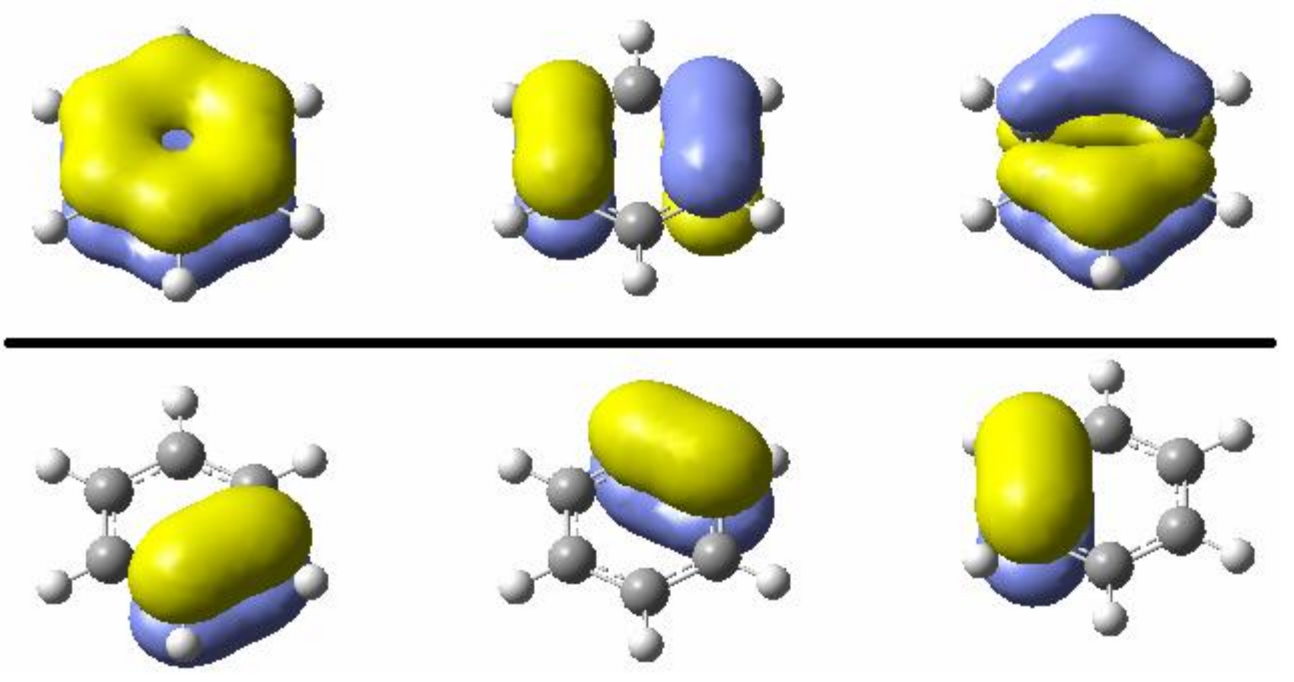
$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & \overline{1s(1)} \\ 1s(2) & \overline{1s(2)} \end{vmatrix}$$

$$\psi \equiv |1s \quad \overline{1s}|$$

Why single determinant ?

- Simple description of electronic wave function
- Simple for computational purposes
- Simple for mathematical transformations
- Simple to extend to correlated methods

Orbitals as single particle wave functions



Orbitals as single particle wave functions

Single particle properties are sum over the molecular orbitals. (Slater-Condon rules)

It significantly provides *live* picture of the molecular orbitals.

How to form orbitals ?

- Solution of Schrödinger equation (impractical)
- Plane wave
- Linear combination of atomic orbitals

Linear Combination of Atomic Orbitals

(LCAO)

One can think of molecular orbitals as summation over atomic orbitals:

$$\psi_j = \sum_i c_{ij}\varphi_i$$

How LCAO coefficients can be chosen?

- Symmetry considerations
- Experimental observations
- Solution of Schrödinger equation
- Energy minimization

Can LCAO provide a solution to the Time-independent Schrödinger equation?

Never *!!!*

Instead, it can approximates the exact solutions.

Variation principle

NATURE, choose the best way:

No trial wave function’s energy is below the exact solution of Schrödinger equation.

It tells us something: Energy is special !

Variation technique

If the energy is upper bound, one may minimize the energy to approach to exact solution.

$$\Psi = f(x, y, z; c_1, c_2, \cdots, c_n)$$

$$\left(\frac{\partial E}{\partial c_k}\right)_{c_{i\neq k}} = 0$$

Linear variation

The coefficients can be chosen to form a linear combination:

$$\Psi = c_1 f_1 + c_2 f_2 + \cdots$$

Remember the LCAO ! $\psi_j = \sum_i c_{ij} \varphi_i$

Can linear variation help to find the LCAO coefficients ?

No !!!

Electronic wave function is not linear with respect to molecular orbitals. Because it must be antisymmetric:

$$\Psi = f(1)g(2) - g(1)f(2)$$

Minimization of determinantal energy

To find approximate solution, one may minimize the energy of determinant.

It is Hartree-Fock (HF) method. Does it have other names?

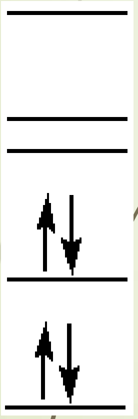
Different terms, pointing to the same concept

- **Self Consistent Field (SCF) approximation**
- **Hartree-Fock (HF) method**
- **Roothan equations**

Different terms, pointing to the same concept

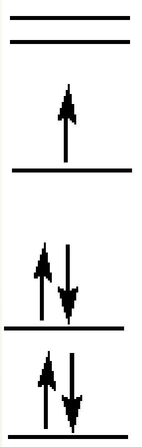
- **SCF: Physical picture**
- **HF: Mathematical picture**
- **Roothan: Matrix representation**

Definition



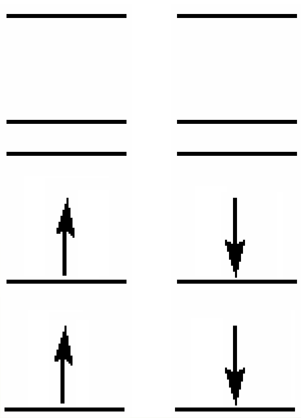
Restricted

Closed-Shell



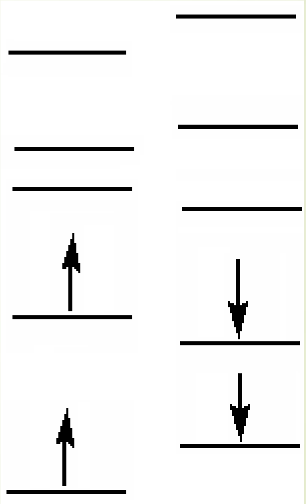
Restricted

Open-Shell



Unrestricted

Closed-Shell



Unrestricted

Open-Shell

Restricted closed-shell Hartree Fock

Electronic wave function is

$$\Psi = |\psi_1 \overline{\psi}_1 \psi_2 \overline{\psi}_2 \cdots \psi_{\frac{N}{2}} \overline{\psi}_{\frac{N}{2}}|$$

where,

$$\psi_j = \sum_i c_{ij} \varphi_i$$

Energy is defined as

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

Wish to find coefficients so that

$$\left(\frac{\partial E}{\partial c_{ij}}\right)_{c_{\mu\nu} \neq c_{ij}} = 0$$

Subject to

$$\langle \Psi | \Psi \rangle = 1$$

Canonical Hartree Fock equations

The energetic minimization reduces to an eigenvalue problem, called as Canonical Hartree-Fock equations:

Fock operator

Orbital energy

$$\hat{F}\psi_a = \varepsilon_a \psi_a$$

Canonical Molecular Orbital

(CMO)

Hartree Fock operator

Restricted closed-shell Hartree Fock operator is defined as:

Core Hamiltonian operator

$$\hat{F} = \hat{H}_{core} + \sum_{a}^{\frac{N}{2}} (2\hat{J}_a - \hat{K}_a)$$

Fock operator

Exchange operator

Coulomb operator

Coulomb and Exchange operators

Coulomb operator:

$$\hat{J}_b(1)\psi_a(1) = \left[\int d\tau_2 \psi_b^*(2)\psi_b(2)\frac{1}{r_{12}}\right]\psi_a(1)$$

Exchange operator:

$$\hat{K}_b(1)\psi_a(1) = \left[\int d\tau_2 \psi_b^*(2)\psi_a(2)\frac{1}{r_{12}}\right]\psi_b(1)$$

Note the difference!

How to solve HF equations?

$$\hat{F}\psi_a = \varepsilon_a\psi_a$$

Operator depends on its eigenvectors!

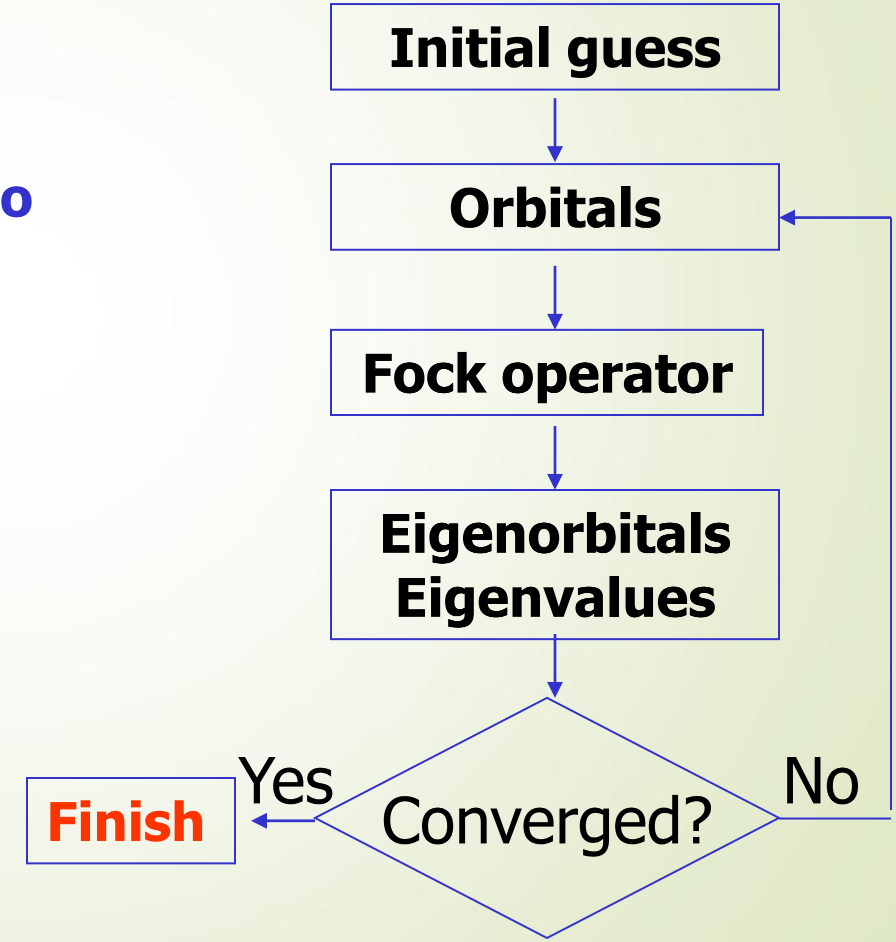
$$\hat{F} = \hat{H}_{core} + \sum_{a}^{\frac{N}{2}}(2\hat{J}_a - \hat{K}_a)$$

$$\hat{J}_b(1)\psi_a(1) = \left[\int d\tau_2\psi_b^*(2)\psi_b(2)\frac{1}{r_{12}}\right]\psi_a(1)$$

$$\hat{K}_b(1)\psi_a(1) = \left[\int d\tau_2\psi_b^*(2)\psi_a(2)\frac{1}{r_{12}}\right]\psi_b(1)$$

Hartree-Fock procedure (Quick glance)

Flowchart of iterative process to solve Hartree-Fock equations:



Roothaan equations

Roothaan equations are matrix representation of Hartree-Fock equations, i.e., the CMOs are considered as superposition over ***base*** elements or ***basis set***. In general, base elements are atomic orbitals (LCAO).

Basis set does not necessarily provides an orthogonal set.

$$\langle \psi_a | \psi_b \rangle \neq \delta_{ab}$$

Matrix elements

Overlap matrix:

$$\mathbf{S}_{\mu\nu} = \int \psi_\mu^*(1)\psi_\nu(1)\,d\mathbf{r}_1$$

Fock matrix:

$$\mathbf{F}_{\mu\nu} = \int \psi_\mu^*(1)\hat{F}\psi_\nu(1)\,d\mathbf{r}_1$$

$$\mathbf{F}_{\mu\nu} = \mathbf{H}_{\mu\nu}^{core} + \mathbf{G}_{\mu\nu}$$

$$\mathbf{G}_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu\,|\,\sigma\lambda) - \tfrac{1}{2}(\mu\lambda\,|\,\sigma\nu)]$$

Matrix elements

Density matrix:

$$\mathbf{P}_{\mu\nu} = 2\sum_{a}^{\frac{N}{2}} \mathbf{C}_{\mu a}\mathbf{C}_{\nu a}^{*}$$

Electron repulsion integral (ERI):

$$(ab\,|\,cd) = \int \varphi_a^*(1)\varphi_b(1)\frac{1}{r_{12}}\varphi_c^*(2)\varphi_d(2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

Coulomb and Exchange matrix elements

Coulomb operator:

$$\mathbf{J}_{ab} = \int \psi_a^*(1)\psi_a(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_b(2)d\tau_1 d\tau_2$$

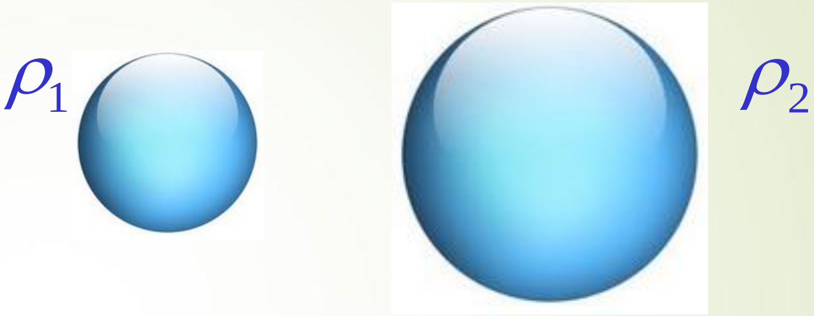
Exchange operator:

$$\mathbf{K}_{ab} = \int \psi_a^*(1)\psi_b(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_a(2)d\tau_1 d\tau_2$$

Note the difference!

Interpretation of Coulomb term

Consider to classical charge clouds:



Classical repulsion potential energy:

$$V = \int \frac{\rho_1(1)\rho_2(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\mathbf{J}_{ab} = \int \boxed{\psi_a^*(1)\psi_a(1)} \boxed{\frac{1}{r_{12}}} \boxed{\psi_b^*(2)\psi_b(2)} d\tau_1 d\tau_2$$

$\mathbf{J}_{ab}$ **is defined as classical repulsion between orbitals *a* and *b*.**

Interpretation of Exchange term

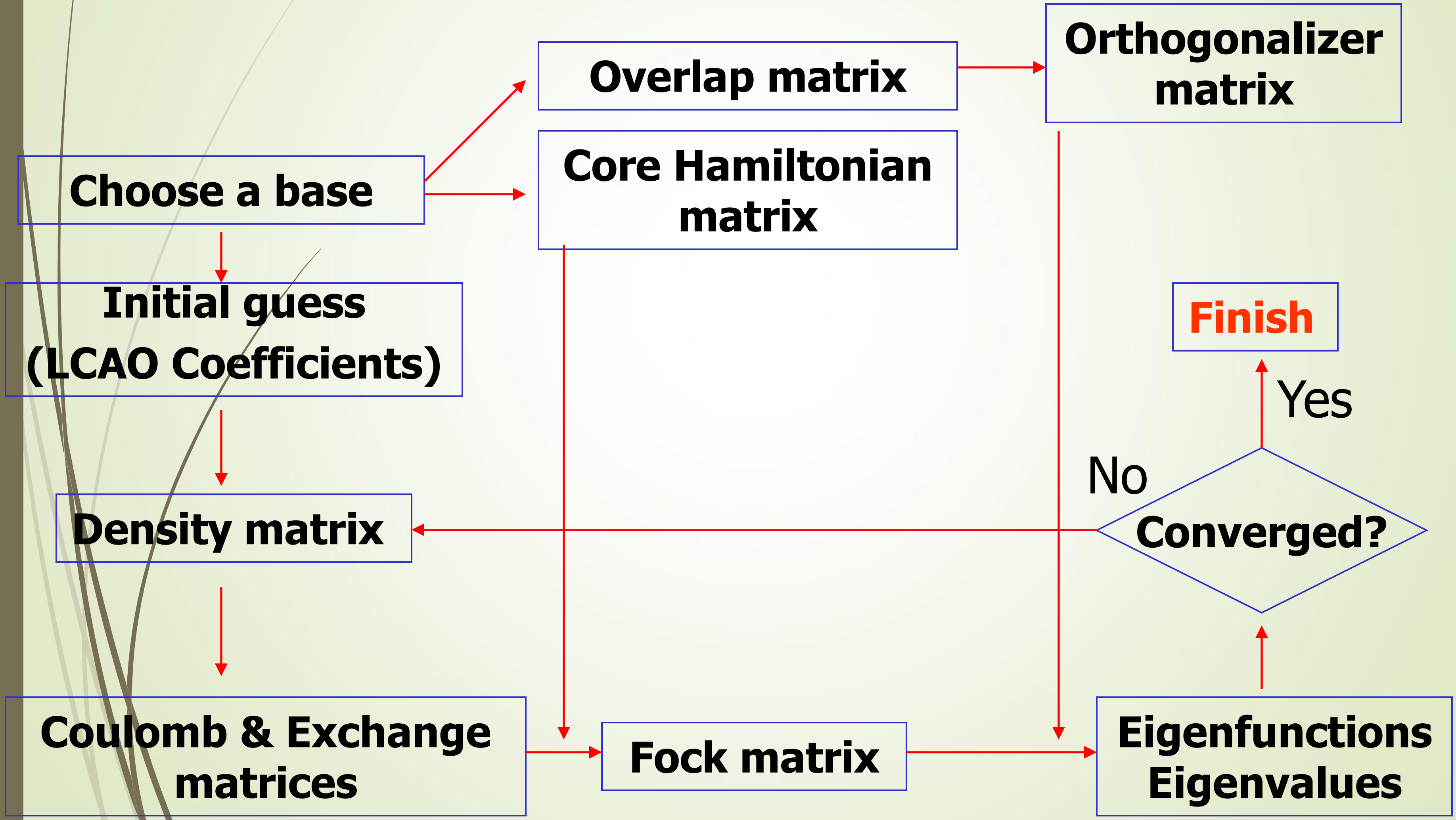
$$\mathbf{J}_{ab} = \int \psi^*\boxed{{}_a(1)\psi_a}(1)\frac{1}{r_{12}}\psi^*\boxed{{}_b(2)\psi_b}(2)\,d\tau_1 d\tau_2$$

$$= \int \rho_a(1)\frac{1}{r_{12}}\rho_b(2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

$$\mathbf{K}_{ab} = \int \psi^*_{\underset{\uparrow}{a}}(1)\psi_{\underset{\uparrow}{b}}(1)\frac{1}{r_{12}}\psi^*_{\underset{\uparrow}{b}}(2)\psi_{\underset{\uparrow}{a}}(2)\,d\tau_1 d\tau_2$$

No classical interpretation for Exchange !!

Hartree-Fock procedure (Matrix approach)



Choose a base

Overlap matrix

Core Hamiltonian matrix

Orthogonalizer matrix

Initial guess (LCAO Coefficients)

Density matrix

Coulomb & Exchange matrices

Fock matrix

Eigenfunctions Eigenvalues

Converged?

No

Yes

Finish

How many Electron repulsion integral are required?

If the base is composed of *n* elements, each matrix will have *n*×*n* dimensions.

$$\mathbf{F}_{\mu\nu} = \int \psi_{\mu}^{*}(1)\hat{F}\psi_{\nu}(1)d\mathbf{r}_1 \longrightarrow n^2 \text{ elements}$$

$$\mathbf{F}_{\mu\nu} = \mathbf{H}_{\mu\nu}^{core} + \mathbf{G}_{\mu\nu} \qquad \frac{n^2}{2} \text{ because F is symmetric}$$

$$\mathbf{G}_{\mu\nu} = \sum_{\boxed{\lambda\sigma}} P_{\lambda\sigma}[\underline{(\mu\nu\,|\,\sigma\lambda)} - \tfrac{1}{2}\underline{(\mu\lambda\,|\,\sigma\nu)}]$$

$$\downarrow$$

$$2n^2 \text{ computation for each element}$$

n^4 Crisis

n^4 **ERI should be computed for each SCF cycle.**

$$(ab\,|\,cd) = \int \varphi_a^*(1)\varphi_b(1)\frac{1}{r_{12}}\varphi_c^*(2)\varphi_d(2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

Fullerene at HF/6-31+G* level contains 1140 basis elements.

1,688,960,160,000 ERIs should be computed !

Handling Electron repulsion integrals

- **Indirect:**

Optimum for too slow CPUs

All ERIs are computed once and stored on physical disk. Restored when needed.

- **In Core:**

Optimum for very small basis sets

All ERIs are computed once and stored on physical memory. Restored when needed.

- **Direct (On the Fly):**

ERI is computed when needed.

Optimum for modern computers

Resources are limited !

No computer can evaluate faster than 1,000,000 ERI per second.

Who can wait 469 hours for C60 ?

1,688,960,160,000

Strategies can be employed to decrease the number of ERI computations:

- ERI symmetry
- Loop over ERIs, rather Fock matrix elements
- Density matrix inspection
- Cauchy-Schwarz inequality
- Orbital rotation
- Sharing common exponent

ERI symmetry

$$(ab\,|\,cd) = \int \varphi_a^*(1)\varphi_b(1)\frac{1}{r_{12}}\varphi_c^*(2)\varphi_d(2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

For real basis sets, all eight ERIs are equal:

$$(ab\,|\,cd) = (ba\,|\,cd) = (ab\,|\,dc) = (ba\,|\,dc)$$

$$= (cd\,|\,ab) = (cd\,|\,ba) = (dc\,|\,ab) = (dc\,|\,ba)$$

How can it help when using DIRECT method?

Equivalent ERIs

$$\mathbf{F}_{\mu\nu} = \mathbf{H}_{\mu\nu}^{core} + \mathbf{G}_{\mu\nu}$$

$$\mathbf{G}_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - \tfrac{1}{2}(\mu\lambda|\sigma\nu)]$$

$$\mathbf{G}_{11} = \sum_{\lambda\sigma} P_{\lambda\sigma}[(11|\sigma\lambda) - \tfrac{1}{2}(1\lambda|\sigma 1)]$$

$$= P_{11}[\boxed{(11|11)} - \tfrac{1}{2}\boxed{(11|11)}] + P_{12}[\boxed{(11|12)} - \tfrac{1}{2}\boxed{(11|21)}]$$

$$+ P_{21}[\boxed{(11|21)} - \tfrac{1}{2}\boxed{(12|11)}] + P_{22}[(11|22) - \tfrac{1}{2}(12|21)]$$

And so on for G_{12}, …

Loop over G is wrong
Loop over ERI is correct

$\mathbf{G}_{11}$, then $\mathbf{G}_{12}$, then $\mathbf{G}_{21}$, then $\mathbf{G}_{22}$

Inefficient, as each step requires 8 ERI computation

$(11|11)$, then $(11|12)$, then $(11|22)$, then

$(12|12)$, then $(22|21)$, then $(22|22)$

At each step, distribute the ERI to G elements

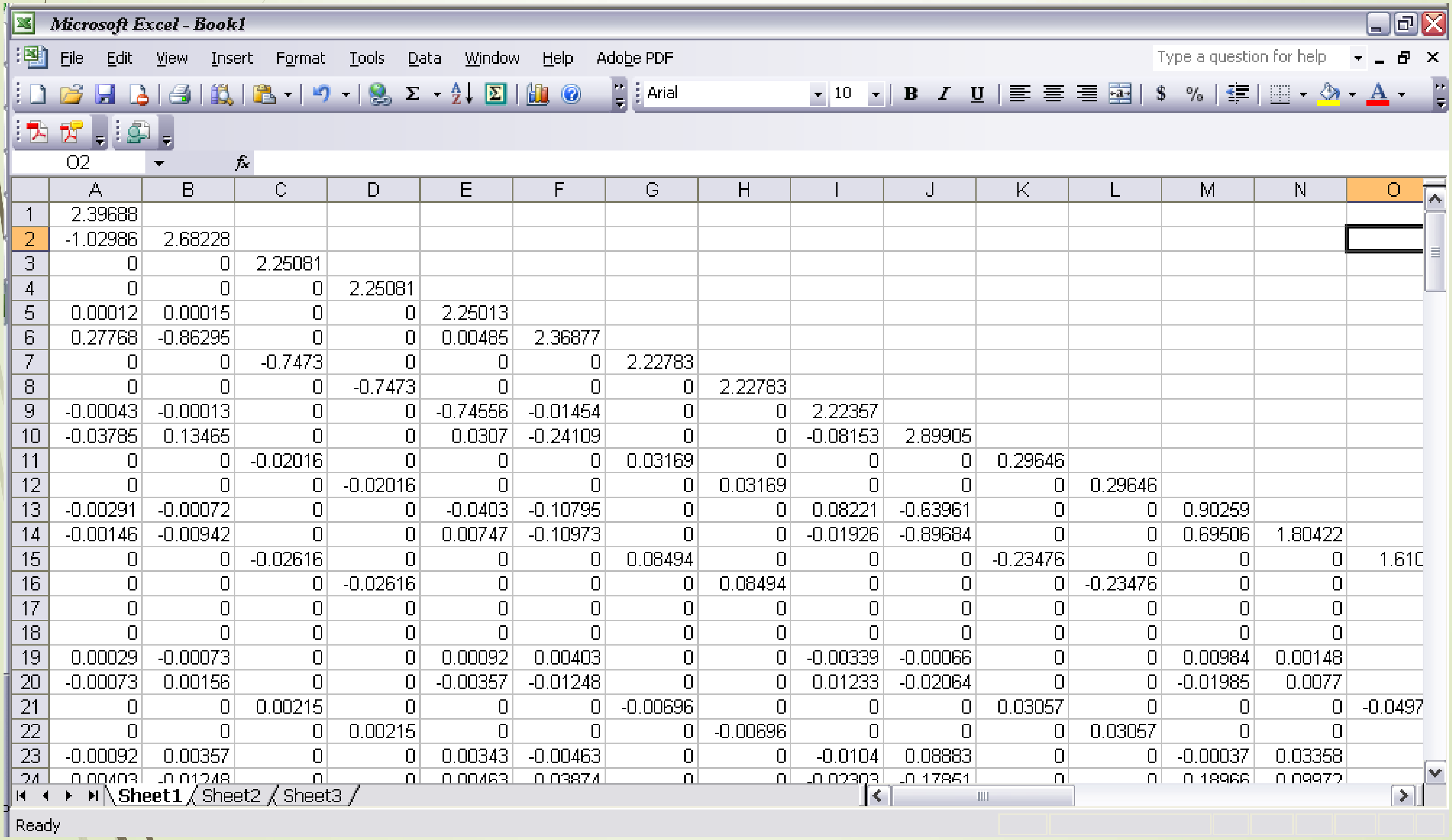
Density matrix inspection

$$
\begin{aligned}
\mathbf{G}_{11} &= \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(11|\sigma\lambda) - \tfrac{1}{2}(1\lambda|\sigma 1)\right] \\
&= \boxed{P_{11}}\left[(11|11) - \tfrac{1}{2}(11|11)\right] + \boxed{P_{12}}\left[(11|12) - \tfrac{1}{2}(11|21)\right] \\
&+ \boxed{P_{21}}\left[(11|21) - \tfrac{1}{2}(12|11)\right] + \boxed{P_{22}}\left[(11|22) - \tfrac{1}{2}(12|21)\right]
\end{aligned}
$$

If one or more of these elements are (almost) zero, why the ERIs should be computed?

Density matrix inspection

Example: Ni_2 density matrix optimized at HF/STO-3G level



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	2.39688														
2	-1.02986	2.68228													
3	0	0	2.25081												
4	0	0	0	2.25081											
5	0.00012	0.00015	0	0	2.25013										
6	0.27768	-0.86295	0	0	0.00485	2.36877									
7	0	0	-0.7473	0	0	0	2.22783								
8	0	0	0	-0.7473	0	0	0	2.22783							
9	-0.00043	-0.00013	0	0	-0.74556	-0.01454	0	0	2.22357						
10	-0.03785	0.13465	0	0	0.0307	-0.24109	0	0	-0.08153	2.89905					
11	0	0	-0.02016	0	0	0	0.03169	0	0	0	0.29646				
12	0	0	0	-0.02016	0	0	0	0.03169	0	0	0	0.29646			
13	-0.00291	-0.00072	0	0	-0.0403	-0.10795	0	0	0.08221	-0.63961	0	0	0.90259		
14	-0.00146	-0.00942	0	0	0.00747	-0.10973	0	0	-0.01926	-0.89684	0	0	0.69506	1.80422	
15	0	0	-0.02616	0	0	0	0.08494	0	0	0	-0.23476	0	0	0	1.61
16	0	0	0	-0.02616	0	0	0	0.08494	0	0	0	-0.23476	0	0	
17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
19	0.00029	-0.00073	0	0	0.00092	0.00403	0	0	-0.00339	-0.00066	0	0	0.00984	0.00148	
20	-0.00073	0.00156	0	0	-0.00357	-0.01248	0	0	0.01233	-0.02064	0	0	-0.01985	0.0077	
21	0	0	0.00215	0	0	0	-0.00696	0	0	0	0.03057	0	0	0	-0.0497
22	0	0	0	0.00215	0	0	0	-0.00696	0	0	0	0.03057	0	0	
23	-0.00092	0.00357	0	0	0.00343	-0.00463	0	0	-0.0104	0.08883	0	0	-0.00037	0.03358	
24	0.00403	-0.01248	0	0	0.00463	0.03874	0	0	-0.02303	-0.17851	0	0	0.18966	0.09972	

Cauchy-Schwarz inequality

$$(\vec{A}\cdot\vec{B})^2 \leq (\vec{A}\cdot\vec{A})(\vec{B}\cdot\vec{B})$$

Square of inner product of two vectors is equal or less than product of their self inner product.

It can be generalized to ERIs:

$$(ab|cd) \leq \sqrt{(ab|ab)(cd|cd)}$$

Integral prescreening

Form g matrix, whose elements are $\mathbf{g}_{ij} = (ij \mid ij)$

$$(ab \mid cd) \leq \sqrt{\mathbf{g}_{ab}\mathbf{g}_{cd}}$$

If $\mathbf{g}_{ab}\mathbf{g}_{cd}$ **is less than a threshold, e.g., 10^{-10}, why should one concern with** $(ab \mid cd)$ **?**

Good News !

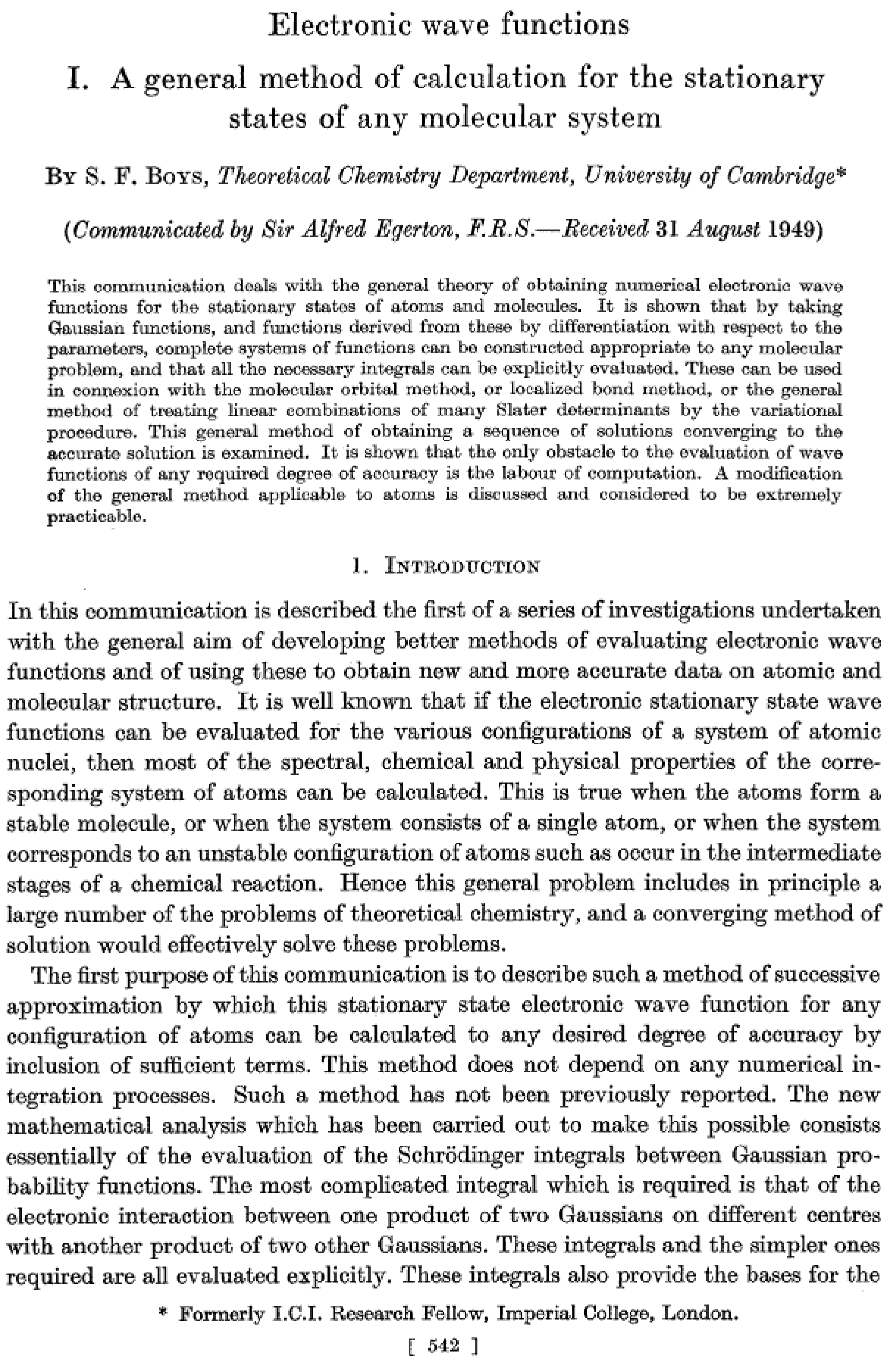
Because of the use of cutoffs, the cost of direct SCF scales with molecular size as $n^{2.7}$ or better, while conventional SCF scales in practice as $n^{3.5}$, where n is the number of basis elements.

H. B. Schlegel and M. J. Frisch, in Theoretical and Computational Models for Organic Chemistry.

S.F. Boys,

Proc. R. Soc. London Ser. A,

200, 542 (1950)



Electronic wave functions

I. A general method of calculation for the stationary states of any molecular system

By S. F. Boys, *Theoretical Chemistry Department, University of Cambridge**

(*Communicated by Sir Alfred Egerton, F.R.S.—Received* 31 *August* 1949)

This communication deals with the general theory of obtaining numerical electronic wave functions for the stationary states of atoms and molecules. It is shown that by taking Gaussian functions, and functions derived from these by differentiation with respect to the parameters, complete systems of functions can be constructed appropriate to any molecular problem, and that all the necessary integrals can be explicitly evaluated. These can be used in connexion with the molecular orbital method, or localized bond method, or the general method of treating linear combinations of many Slater determinants by the variational procedure. This general method of obtaining a sequence of solutions converging to the accurate solution is examined. It is shown that the only obstacle to the evaluation of wave functions of any required degree of accuracy is the labour of computation. A modification of the general method applicable to atoms is discussed and considered to be extremely practicable.

1. INTRODUCTION

In this communication is described the first of a series of investigations undertaken with the general aim of developing better methods of evaluating electronic wave functions and of using these to obtain new and more accurate data on atomic and molecular structure. It is well known that if the electronic stationary state wave functions can be evaluated for the various configurations of a system of atomic nuclei, then most of the spectral, chemical and physical properties of the corresponding system of atoms can be calculated. This is true when the atoms form a stable molecule, or when the system consists of a single atom, or when the system corresponds to an unstable configuration of atoms such as occur in the intermediate stages of a chemical reaction. Hence this general problem includes in principle a large number of the problems of theoretical chemistry, and a converging method of solution would effectively solve these problems.

The first purpose of this communication is to describe such a method of successive approximation by which this stationary state electronic wave function for any configuration of atoms can be calculated to any desired degree of accuracy by inclusion of sufficient terms. This method does not depend on any numerical integration processes. Such a method has not been previously reported. The new mathematical analysis which has been carried out to make this possible consists essentially of the evaluation of the Schrödinger integrals between Gaussian probability functions. The most complicated integral which is required is that of the electronic interaction between one product of two Gaussians on different centres with another product of two other Gaussians. These integrals and the simpler ones required are all evaluated explicitly. These integrals also provide the bases for the

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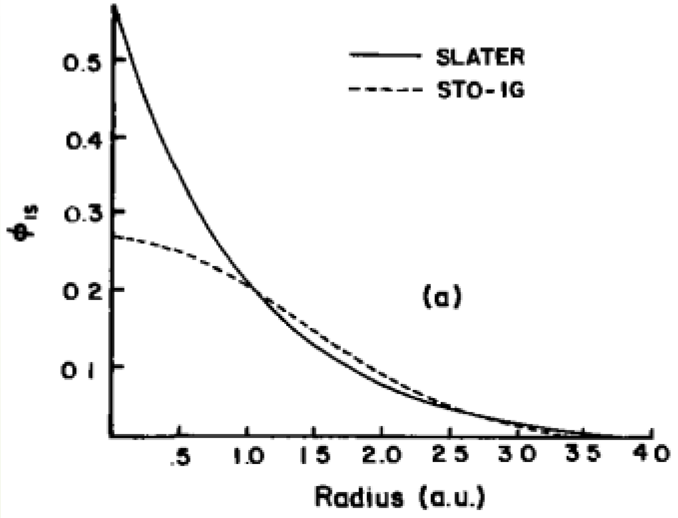
* Formerly I.C.I. Research Fellow, Imperial College, London.

Gaussian type orbitals (GTO)

$$G(\mathbf{r};\underset{\text{Exponent}}{\underbrace{\zeta}},\overset{\text{Angular momentum}}{\overbrace{\mathbf{n}}},\underset{\text{Center}}{\underbrace{\mathbf{R}}})=(x-R_x)^{n_x}(y-R_y)^{n_y}(z-R_z)^{n_z}e^{-\zeta(\mathbf{r}-\mathbf{R})^2}$$

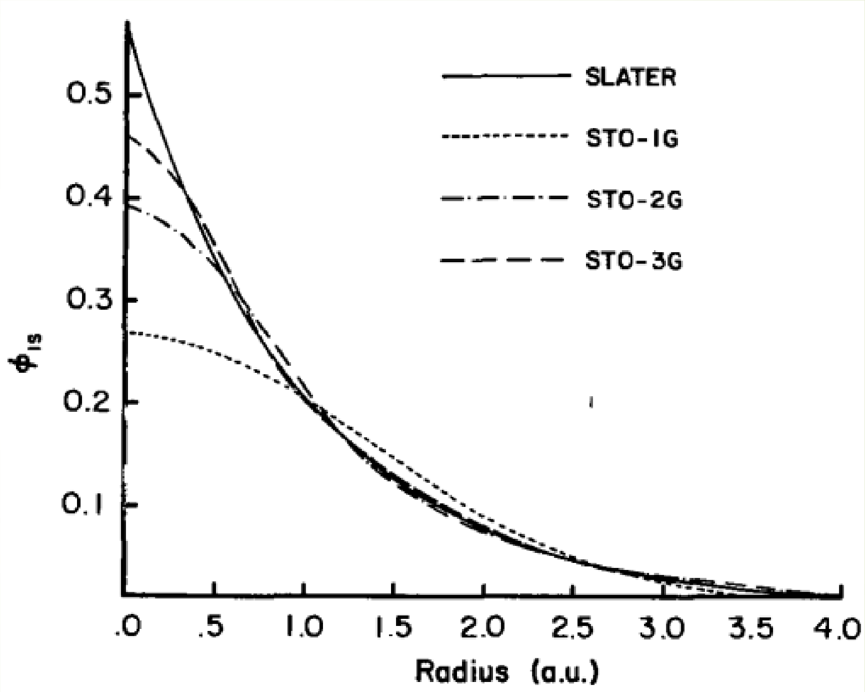
GTOs are extremely efficient candidates for Slater type orbitals.

But they are different:



Contracted orbitals

A Slater type orbital can be fitted to a linear combination of GTOs.



$$\phi_{1s}^{CGF}(\zeta = 1.24, \text{STO-3G}) = 0.444635\phi_{1s}^{GF}(0.168856) + 0.535328\phi_{1s}^{GF}(0.623913) + 0.154329\phi_{1s}^{GF}(3.42525)$$

Contraction coefficients

ERI evaluation over 1*s* GTOs

$$(\mathbf{0}_A\mathbf{0}_B|\mathbf{0}_C\mathbf{0}_D) = (\mathbf{0}_A\|\mathbf{0}_B)(\mathbf{0}_C\|\mathbf{0}_B)\frac{2}{\pi^{\frac{1}{2}}}\int_0^{+\infty}\left(\frac{\rho}{\rho+u^2}\right)^{\frac{3}{2}} e^{-\frac{\rho u^2}{\rho+u^2}(\mathbf{P}-\mathbf{Q})^2}\,du$$

1s GTOs centered at A, B, C, D

Overlap integral

can be transformed to

$$F_m(x) = \int_0^1 t^{2m} e^{-xt^2}\,dt$$

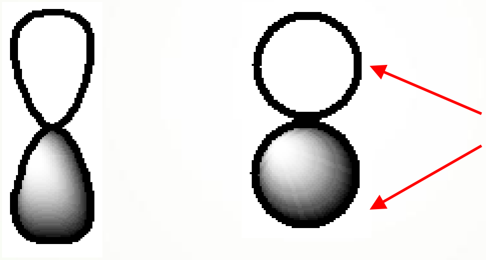
(Incomplete Gamma Function)

where,

$$\mathbf{P} = \frac{\zeta_A\mathbf{A}+\zeta_B\mathbf{B}}{\zeta_A+\zeta_B} \quad \mathbf{Q} = \frac{\zeta_C\mathbf{C}+\zeta_D\mathbf{D}}{\zeta_C+\zeta_D} \quad \rho = \frac{(\zeta_A+\zeta_B)(\zeta_C+\zeta_D)}{\zeta_A+\zeta_B+\zeta_C+\zeta_D}$$

Transformation to 1*s* orbitals

It is possible to rewrite (approximate) a *p*-type GTO as linear combination of off-center *s*-type GTOs:



True p-type GTO

Two *s*-type GTO

$$p = 0.98 s_a + 0.98 s_b$$

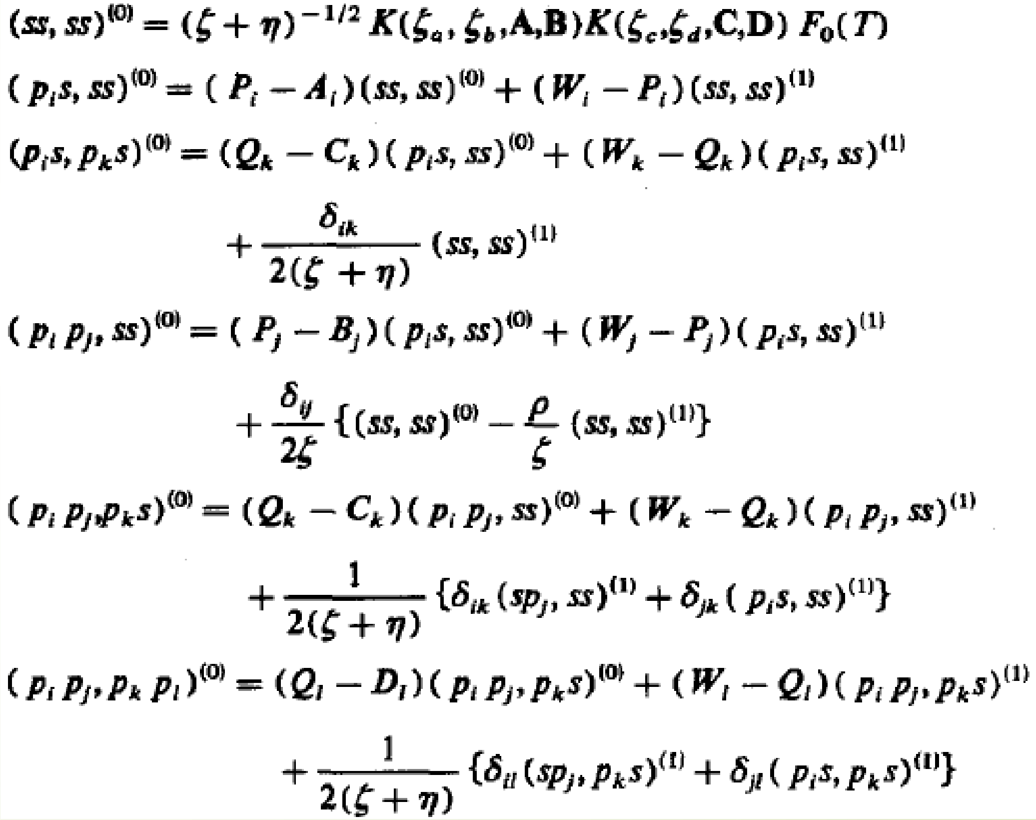
$$(\varphi_1 \varphi_2 \,|\, \varphi_3 p) = 0.98 (\varphi_1 \varphi_2 \,|\, \varphi_3 s_a) + 0.98 (\varphi_1 \varphi_2 \,|\, \varphi_3 s_b)$$

More GTOs to combine, more accurate fitting !

Using table of ERIs

One can formulate ERIs with all possible angular momenta before implementation into the code.

The number of possible ERIs for *d* orbitals are significantly large!



$$(ss, ss)^{(0)} = (\zeta + \eta)^{-1/2} K(\zeta_a, \zeta_b, \mathbf{A}, \mathbf{B}) K(\zeta_c, \zeta_d, \mathbf{C}, \mathbf{D})\, F_0(T)$$

$$(p_i s, ss)^{(0)} = (P_i - A_i)(ss, ss)^{(0)} + (W_i - P_i)(ss, ss)^{(1)}$$

$$(p_i s, p_k s)^{(0)} = (Q_k - C_k)(p_i s, ss)^{(0)} + (W_k - Q_k)(p_i s, ss)^{(1)} + \frac{\delta_{ik}}{2(\zeta + \eta)}(ss, ss)^{(1)}$$

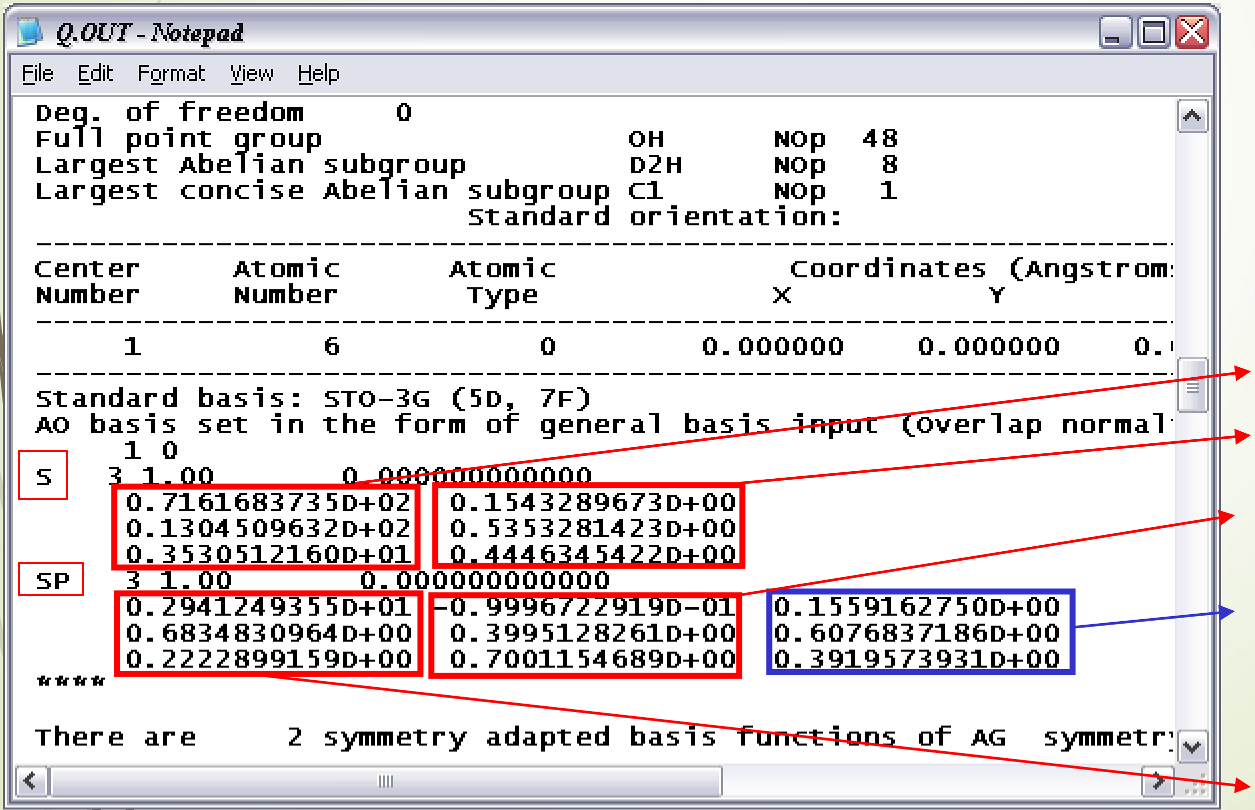
$$(p_i p_j, ss)^{(0)} = (P_j - B_j)(p_i s, ss)^{(0)} + (W_j - P_j)(p_i s, ss)^{(1)} + \frac{\delta_{ij}}{2\zeta}\left\{(ss, ss)^{(0)} - \frac{\rho}{\zeta}(ss, ss)^{(1)}\right\}$$

$$(p_i p_j, p_k s)^{(0)} = (Q_k - C_k)(p_i p_j, ss)^{(0)} + (W_k - Q_k)(p_i p_j, ss)^{(1)} + \frac{1}{2(\zeta + \eta)}\left\{\delta_{ik}(sp_j, ss)^{(1)} + \delta_{jk}(p_i s, ss)^{(1)}\right\}$$

$$(p_i p_j, p_k p_l)^{(0)} = (Q_l - D_l)(p_i p_j, p_k s)^{(0)} + (W_l - Q_l)(p_i p_j, p_k s)^{(1)} + \frac{1}{2(\zeta + \eta)}\left\{\delta_{il}(sp_j, p_k s)^{(1)} + \delta_{jl}(p_i s, p_k s)^{(1)}\right\}$$

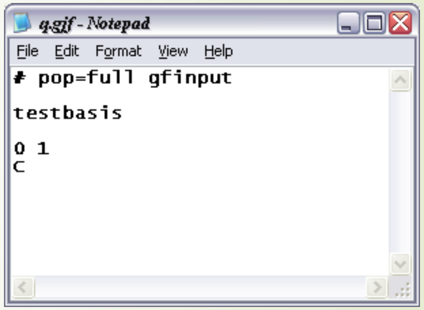
Sharing common exponents

Have you ever encountered *sp* shells? It makes ERI computations more efficient.



```
 Deg. of freedom      0
 Full point group                 OH      NOp  48
 Largest Abelian subgroup         D2H     NOp   8
 Largest concise Abelian subgroup C1      NOp   1
                        Standard orientation:
 ---------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstrom
 Number     Number       Type             X           Y
 ---------------------------------------------------------------
      1          6           0        0.000000    0.000000    0.
 ---------------------------------------------------------------
 Standard basis: STO-3G (5D, 7F)
 AO basis set in the form of general basis input (Overlap normal
      1 0
 S    3 1.00       0.000000000000
      0.7161683735D+02  0.1543289673D+00
      0.1304509632D+02  0.5353281423D+00
      0.3530512160D+01  0.4446345422D+00
 SP   3 1.00       0.000000000000
      0.2941249355D+01 -0.9996722919D-01  0.1559162750D+00
      0.6834830964D+00  0.3995128261D+00  0.6076837186D+00
      0.2222899159D+00  0.7001154689D+00  0.3919573931D+00
 ****

 There are      2 symmetry adapted basis functions of AG   symmetr
```



```
# pop=full gfinput

testbasis

0 1
C
```

Exponents

Coefficients

s shell

p shell

Shared Exponents

SCF techniques

- **Intrinsic convergence**
- **Oscillation damping**
- **Interpolation of the density matrix**
- **direct inversion of the iterative subspace**
- **Quadratic convergence**

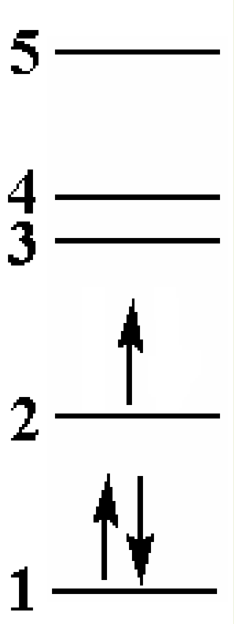
SCF Energy

Electronic energy can be simply expressed in terms of core Hamiltonian, Coulomb and exchange terms.

Core Hamiltonian: all electrons

Coulomb: between all electrons

Exchange: between the same spin electrons

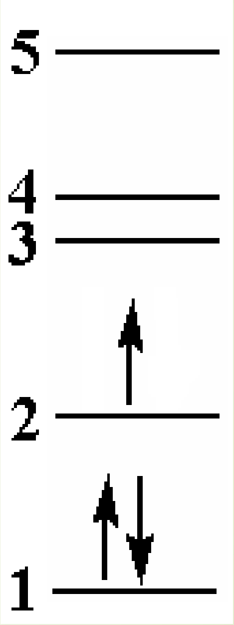


$$E = 2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$$

SCF Energy

Literature: HF method does not include non-classical terms for electron-electron repulsion energy, i.e., opposite spin electrons are not correlated within HF energy.

Correlated methods includes the correlation for both opposite and same spin electrons.



$$E = 2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$$

Example: Hydrogen molecule at Restricted Hartree-Fock (RHF) level

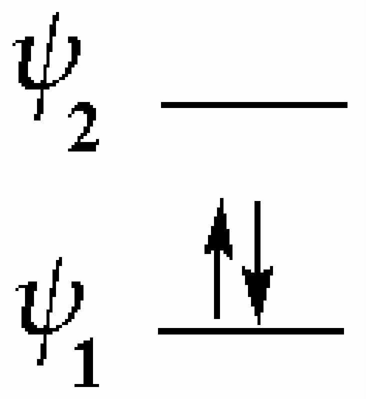
Hydrogen molecule is the simplest diatomic system with non-zero electron correlation energy.

$$\Psi = |\psi_1\overline{\psi}_1|$$

$$E = 2h_{11} + J_{11}$$

or

$$E = 2h_{\sigma\sigma} + J_{\sigma\sigma}$$



Anti-Bonding orbital

Bonding orbital

Example: Hydrogen molecule

At large distances, it is expected that $E_{H_2} = 2E_H$

Let’s examine SCF energy of H2 at large distances:

$$h_{\sigma\sigma} = h_{1s1s}$$

$$J_{\sigma\sigma} = \tfrac{1}{2} J_{1s1s} = \tfrac{1}{2}(1s1s\,|\,1s1s)$$

$$(\lim_{R\to+\infty} E_{H_2}) - 2E_H = \tfrac{1}{2}(1s1s\,|\,1s1s) \neq 0$$

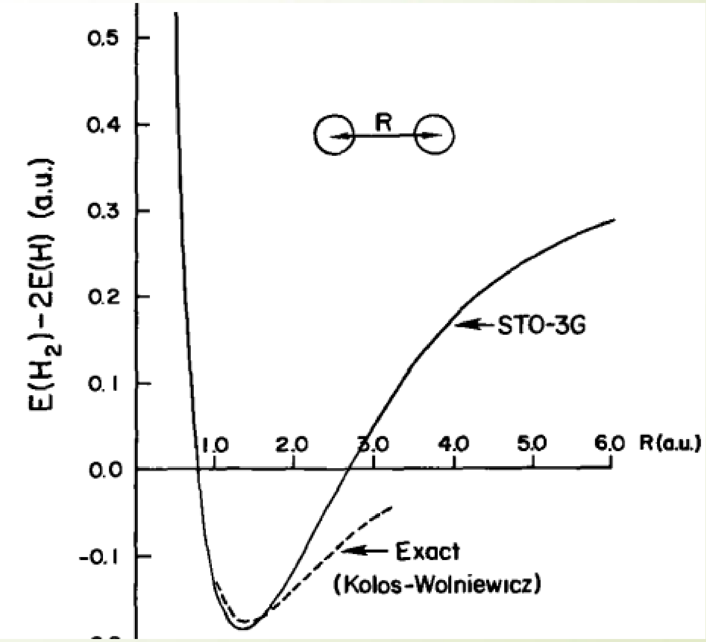
Example: Hydrogen molecule

Relative error of energy at large distances is significant:

$$2E_H = -0.9332\ a.u.$$

$$\tfrac{1}{2}(1s1s\,|\,1s1s) = 0.3873\ a.u.$$

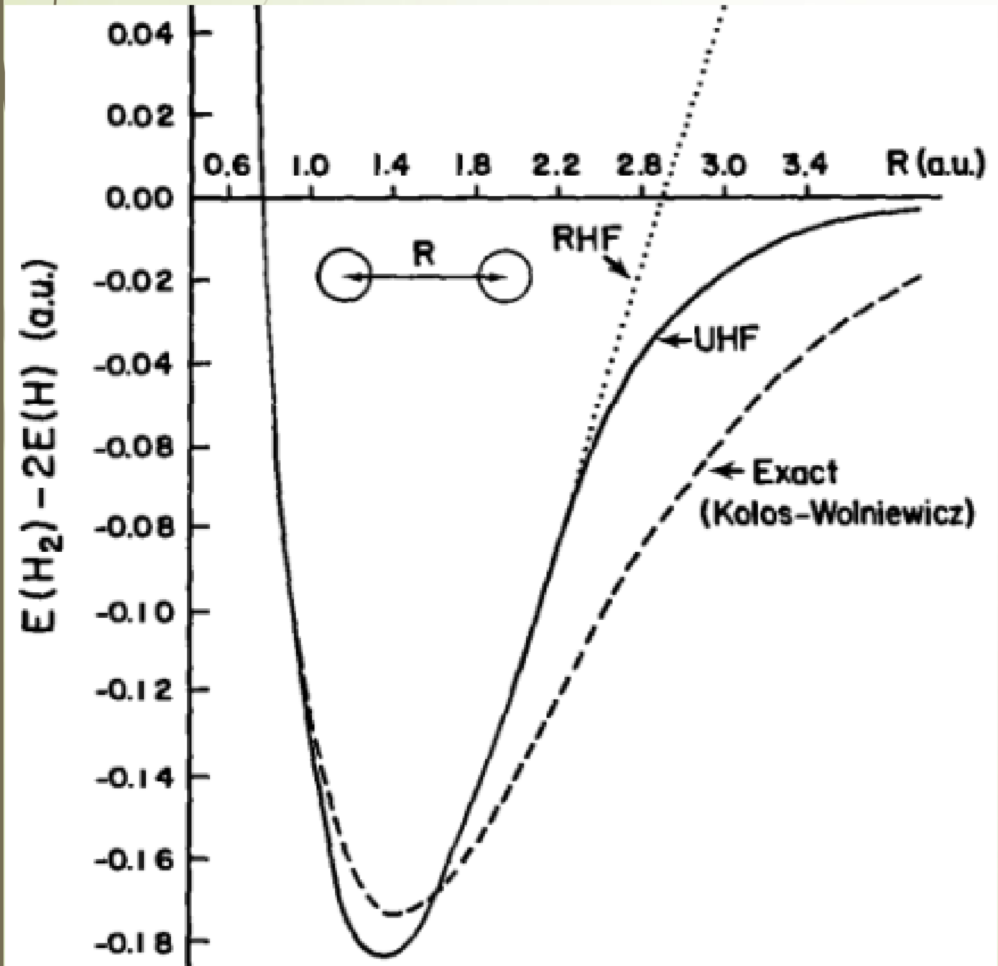
Large error !!



How about the error at equilibrium geometry?

4% error for bond length

Example: Unrestricted hydrogen molecule



$$\Psi = |\psi_a \overline{\psi}_b|$$

Unrestricted Hartree-Fock (UHF) potential energy curve for hydrogen molecule predicts better energies than RHF at large distances

Energy is correct, but wave function not! It is not a pure singlet spin state.

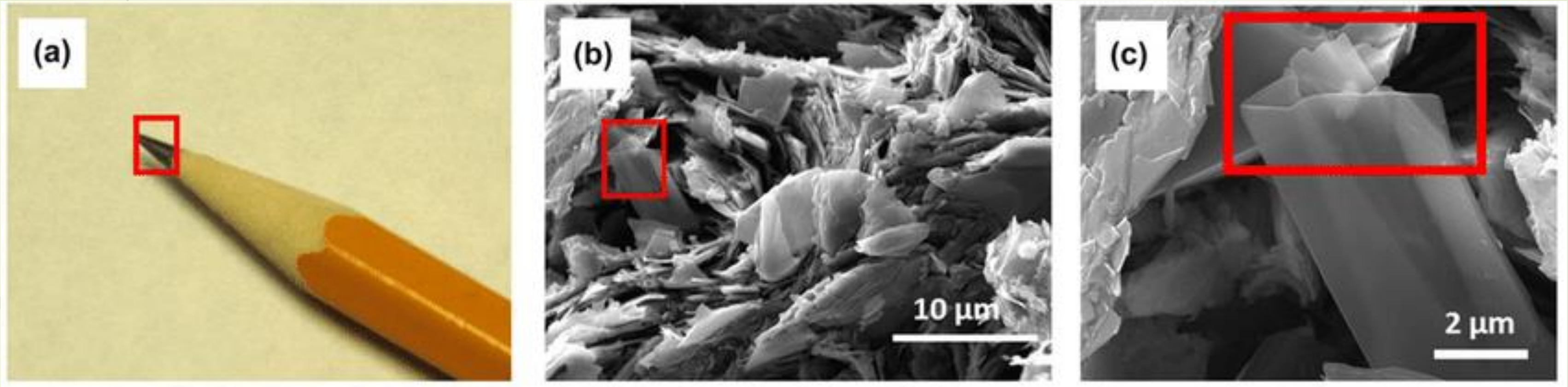
$$\hat{S}^2\Psi \neq \lambda\Psi$$

Example: SCF bond length of some ten electron molecule

It seems that SCF well predicts the bond lengths!

Basis set	CH4	NH3	H2O	FH
STO-3G	2.047	1.952	1.871	1.807
4-31G	2.043	1.873	1.797	1.742
Near-HF-Limit	2.048	1.890	1.776	1.696
Experiment	2.050	1.912	1.809	1.733

Nice pictures vanish when zoom in!



Is Slater determinant the right wavefunction?


Thank you