

Solution of the Electronic Schrödinger Equation

Using Basis Sets to Solve the Hartree-Fock Equations

Comments on Hartree-Fock Theory

■ Reasonable Description of Electronic Structure

- Most atoms
- Many molecules near their equilibrium geometries (although there are exceptions)

■ Basis for More Accurate Calculations

- HF is zero-order wave function used in many more accurate models of the electronic structure of atoms and molecules that include electron correlation
 - Configuration interaction
 - Perturbation theory
 - Coupled cluster theory

Hartree-Fock Wave Function and Energy

Just to review, the Hartree-Fock (HF) wave function for N_e electrons is

$$\begin{aligned}\Psi_e(1,2,3,\dots,N_e) &= \hat{\mathcal{A}}\bar{\phi}_a(1)\bar{\phi}_b(2)\bar{\phi}_c(3)\cdots\bar{\phi}_n(N_e) \\ &= \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \bar{\phi}_a(1) & \bar{\phi}_a(2) & \cdots & \bar{\phi}_a(N_e) \\ \bar{\phi}_b(1) & \bar{\phi}_b(2) & \cdots & \bar{\phi}_b(N_e) \\ \vdots & \vdots & \ddots & \vdots \\ \bar{\phi}_n(1) & \bar{\phi}_n(2) & \cdots & \bar{\phi}_n(N_e) \end{vmatrix}\end{aligned}$$

where $\bar{\phi}_i$ is a spin orbital, *i.e.*, a combination of a spatial function and a spin function. The energy of the HF wave function is:

$$\begin{aligned}E &= \sum_{i=1}^{N_e} h_{\bar{i}\bar{i}} + \sum_{i=1}^{N_e} \sum_{j=i+1}^{N_e} (J_{\bar{i}\bar{j}} - K_{\bar{i}\bar{j}}) \\ &= \sum_{i=1}^{N_e} h_{\bar{i}\bar{i}} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} (J_{\bar{i}\bar{j}} - K_{\bar{i}\bar{j}})\end{aligned}$$

Hartree-Fock Equations

The optimum orbitals to use in the HF wave function are the solutions of the HF equations

$$\hat{f}^{\text{HF}} \bar{\phi}_i = \left[\hat{h} + \sum_{k=1}^{N_e} (\hat{J}_{\bar{k}} - \hat{K}_{\bar{k}}) \right] \bar{\phi}_i = \varepsilon_{ii} \bar{\phi}_i$$

where

$$\hat{h} = -\frac{1}{2} \nabla_1^2 - \sum_{I=1}^{N_N} \frac{Z_I}{r_{I1}}$$

One electron operator:
(kinetic energy plus nuclear attraction)

$$\hat{J}_{\bar{k}} = \int dr_2 \frac{\bar{\phi}_{\bar{k}}^*(2) \bar{\phi}_{\bar{k}}(2)}{r_{12}}$$

Coulomb operator

$$\hat{K}_{\bar{k}} = \int dr_2 \frac{\bar{\phi}_{\bar{k}}^*(2) \hat{p}_{12} \bar{\phi}_{\bar{k}}(2)}{r_{12}}$$

Exchange operator
(\hat{p}_{12} is the permutation operator)

RHF Equations for Closed Shell Singlet States

For a singlet state with all of the orbitals doubly occupied, $N_e = 2n$, and the HF wave function is

$${}^1\Psi_e^{\text{RHF}}(1, 2, 3, \dots, N_e) = \hat{\mathcal{A}}\phi_a\phi_a\phi_b\phi_b\cdots\phi_n\phi_n\alpha\beta\alpha\beta\cdots\alpha\beta$$

The HF equations are

$$\hat{f}^{\text{RHF}}\phi_i = \left[\hat{h} + \sum_{k=1}^n (2\hat{J}_k - \hat{K}_k) \right] \phi_i = \varepsilon_i\phi_i$$

These are the *closed shell Restricted Hartree-Fock* (RHF) wave function and equations.

For atoms and diatomic molecules, the integro-differential RHF equations can be solved by finite difference or finite element methods. For polyatomic molecules, these approaches pose significant mathematical problems and the equations have traditionally been solved using basis set expansion methods.

Basis Set Expansion Method

The orbital ϕ_i in the RHF equation is a function of a set of one-electron variables, (x_1, y_1, z_1) , and thus it can be represented by an expansion in a basis set:

$$\phi_i = \sum_{v=1}^{N_{bf}} \chi_v c_{vi}$$

where χ_v is also a function of (x_1, y_1, z_1) .

If the basis set, $\{\chi_v\}$, is a *complete set*, we will obtain an exact solution of the RHF equations. For practical reasons, it is not possible to use a complete basis set, so an error is always associated with the use of this approach. However, as the basis set approaches completeness, this error becomes vanishingly small.

Matrix Hartree-Fock Equations

Using the basis set expansion method, the RHF equations become

$$\hat{f}^{\text{RHF}} \phi_i = \hat{f}^{\text{RHF}} \sum_{v=1}^{N_{bf}} \chi_v c_{vi} = \varepsilon_i \phi_i = \varepsilon_i \sum_{v=1}^{N_{bf}} \chi_v c_{vi}$$

$$\sum_{v=1}^{N_{bf}} \hat{f}^{\text{RHF}} \chi_v c_{vi} = \varepsilon_i \sum_{v=1}^{N_{bf}} \chi_v c_{vi}$$

If we now project χ_μ^* onto these equations and integrate, we obtain

$$\sum_{v=1}^{N_{bf}} \int d\mathbf{r}_1 \chi_\mu^* \hat{f}^{\text{RHF}} \chi_v c_{vi} = \varepsilon_i \sum_{v=1}^{N_{bf}} \int d\mathbf{r}_1 \chi_\mu^* \chi_v c_{vi}$$

$$\sum_{v=1}^{N_{bf}} F_{\mu v}^{\text{RHF}} c_{vi} = \varepsilon_i \sum_{v=1}^{N_{bf}} S_{\mu v} c_{vi}$$

Since these equations must hold for all μ , they reduce to the matrix equation

$$\mathbf{F}^{\text{RHF}} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\varepsilon}$$

Matrix Hartree-Fock Equations

(cont'd)

In the matrix RHF equations

$$\mathbf{F} = \begin{pmatrix} F_{11}^{\text{RHF}} & F_{12}^{\text{RHF}} & \cdots & F_{1K}^{\text{RHF}} \\ F_{21}^{\text{RHF}} & F_{22}^{\text{RHF}} & \cdots & F_{2K}^{\text{RHF}} \\ \vdots & \vdots & \vdots & \vdots \\ F_{K1}^{\text{RHF}} & F_{K2}^{\text{RHF}} & \cdots & F_{KK}^{\text{RHF}} \end{pmatrix}$$

Fock Matrix

$$\mathbf{S} = \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1K} \\ S_{21} & S_{22} & \cdots & S_{2K} \\ \vdots & \vdots & \vdots & \vdots \\ S_{K1} & S_{K2} & \cdots & S_{KK} \end{pmatrix}$$

Overlap Matrix

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1K} \\ c_{21} & c_{22} & \cdots & c_{2K} \\ \vdots & \vdots & \vdots & \vdots \\ c_{K1} & c_{K2} & \cdots & c_{KK} \end{pmatrix}$$

Coefficient Matrix

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{11} & 0 & \cdots & 0 \\ 0 & \varepsilon_{22} & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \varepsilon_{KK} \end{pmatrix}$$

Orbital Energy Matrix
(diagonal)

Kinetic Energy & Nuclear Attraction Matrix Elements

The one-electron contributions to the Fock matrix are

$$F_{\mu\nu}^{\text{RHF}} = \int d\mathbf{r}_1 \chi_{\mu}^* \hat{h} \chi_{\nu} + \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^* (2\hat{J}_k - \hat{K}_k) \chi_{\nu}$$

$$\int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \left(-\frac{1}{2} \nabla_1^2 \right) \chi_{\nu}(\mathbf{r}_1)$$

$= T_{\mu\nu}$

kinetic energy
terms

$$\sum_{I=1}^{N_N} \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \left(-\frac{Z_I}{r_{I1}} \right) \chi_{\nu}(\mathbf{r}_1)$$

$= V_{\mu\nu}^{\text{nucl}}$

nuclear attraction
terms

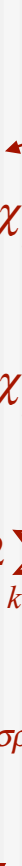
Since there are N_{bf} basis functions in the basis set, N_{bf}^2 one-electron integrals of each type must be computed to construct the one electron matrix. Actually, since the kinetic and nuclear attraction operators are hermitian, only $N_{bf}(N_{bf}+1)/2$ integrals must be computed.

Coulomb Matrix Elements

The two-electron Coulomb contribution to the Fock matrix is

$$F_{\mu\nu}^{\text{RHF}} = \int d\mathbf{r}_1 \chi_{\mu}^* \hat{h} \chi_{\nu} + \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^* (2\hat{J}_k - \hat{K}_k) \chi_{\nu}$$

$$\begin{aligned}
 2 \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \hat{J}_k(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) &= 2 \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \left(\int d\mathbf{r}_2 \frac{\phi_k^*(\mathbf{r}_2) \phi_k(\mathbf{r}_2)}{r_{12}} \right) \chi_{\nu}(\mathbf{r}_1) \\
 &= 2 \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \left(\sum_{\sigma=1}^K \sum_{\rho=1}^K c_{\sigma k}^* c_{\rho k} \int d\mathbf{r}_2 \frac{\chi_{\sigma}^*(\mathbf{r}_2) \chi_{\rho}(\mathbf{r}_2)}{r_{12}} \right) \chi_{\nu}(\mathbf{r}_1) \\
 &= \sum_{\sigma=1}^K \sum_{\rho=1}^K \left(2 \sum_{k=1}^n c_{\sigma k}^* c_{\rho k} \right) \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_{\mu}^*(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) \chi_{\sigma}^*(\mathbf{r}_2) \chi_{\rho}(\mathbf{r}_2)}{r_{12}} \\
 &= \sum_{\sigma=1}^K \sum_{\rho=1}^K D_{\sigma\rho} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_{\mu}^*(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) \chi_{\sigma}^*(\mathbf{r}_2) \chi_{\rho}(\mathbf{r}_2)}{r_{12}} = \sum_{\sigma=1}^K \sum_{\rho=1}^K D_{\sigma\rho} [\mu\nu | \sigma\rho]
 \end{aligned}$$



 density matrix

Exchange Matrix Elements

The two-electron exchange contribution to the Fock matrix is

$$F_{\mu\nu}^{\text{RHF}} = \int d\mathbf{r}_1 \chi_{\mu}^* \hat{h} \chi_{\nu} + \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^* (2\hat{J}_k - \hat{K}_k) \chi_{\nu}$$

$$\begin{aligned} \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \hat{K}_k(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) &= \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \left(\int d\mathbf{r}_2 \frac{\phi_k^*(\mathbf{r}_2) \hat{p}_{12} \phi_k(\mathbf{r}_2)}{r_{12}} \right) \chi_{\nu}(\mathbf{r}_1) \\ &= \sum_{k=1}^n \int d\mathbf{r}_1 \chi_{\mu}^*(\mathbf{r}_1) \left(\sum_{\sigma=1}^K \sum_{\rho=1}^K c_{\sigma k}^* c_{\rho k} \int d\mathbf{r}_2 \frac{\chi_{\sigma}^*(\mathbf{r}_2) \hat{p}_{12} \chi_{\rho}(\mathbf{r}_2)}{r_{12}} \right) \chi_{\nu}(\mathbf{r}_1) \\ &= \sum_{\sigma=1}^K \sum_{\rho=1}^K \left(\sum_{k=1}^n c_{\sigma k}^* c_{\rho k} \right) \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_{\mu}^*(\mathbf{r}_1) \chi_{\rho}(\mathbf{r}_1) \chi_{\sigma}^*(\mathbf{r}_2) \chi_{\nu}(\mathbf{r}_2)}{r_{12}} \\ &= \sum_{\sigma=1}^K \sum_{\rho=1}^K \frac{1}{2} D_{\sigma\rho} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_{\mu}^*(\mathbf{r}_1) \chi_{\rho}(\mathbf{r}_1) \chi_{\sigma}^*(\mathbf{r}_2) \chi_{\nu}(\mathbf{r}_2)}{r_{12}} = \frac{1}{2} \sum_{\sigma=1}^K \sum_{\rho=1}^K D_{\sigma\rho} [\mu\rho | \sigma\nu] \end{aligned}$$

There are $O(N_{bf}^4/8)$ two-electron integrals, $[\mu\nu|\sigma\rho]$. The cost of computing these integrals dominates the cost of the integral calculation.

Matrix Elements of the Fock Operator

Combining the one-electron and the two-electron terms, the Fock matrix elements become

$$\begin{aligned} F_{\mu\nu}^{\text{RHF}} &= T_{\mu\nu} + V_{\mu\nu}^{\text{nucl}} + \sum_{\sigma=1}^{N_{\text{bf}}} \sum_{\rho=1}^{N_{\text{bf}}} D_{\sigma\rho} \left([\mu\nu | \sigma\rho] - \frac{1}{2} [\mu\rho | \sigma\nu] \right) \\ &= T_{\mu\nu} + V_{\mu\nu}^{\text{nucl}} + G_{\mu\nu} \end{aligned}$$

So, the problem reduces to calculating the one-electron kinetic energy, nuclear attraction and two-electron $1/r_{12}$ integrals over the selected set of basis functions, $\{\chi_{\mu}\}$, and then solving the matrix equation

$$\mathbf{F}^{\text{RHF}} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\varepsilon}$$

Solution of this equation involves transformation to an orthonormal basis set (the $\{\chi_{\mu}\}$ are usually normalized but not orthogonal) and then diagonalization of the resulting matrix. The eigenvalues of the matrix correspond to the orbital energies, $\{\varepsilon_{ii}\}$, and the eigenvectors, transformed back to the original basis set, correspond to the expansion coefficients, $\{c_{vi}\}$.

RHF Energy

The electronic contribution to the total RHF energy is

$$\begin{aligned} E_e^{\text{RHF}} &= 2 \sum_{i=1}^n h_{ii} + \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij}) \\ &= 2 \sum_{i=1}^n D_{\mu\nu} (T_{\mu\nu} + V_{\mu\nu}) + \sum_{i=1}^n \sum_{j=1}^n D_{\mu\nu} (2[\mu\nu|\sigma\rho] - [\mu\rho|\sigma\nu]) \end{aligned}$$

The nuclear contribution is

$$E_N = \sum_{I=1}^{N_N} \sum_{J=I}^{N_N} \frac{Z_I Z_J}{R_{IJ}}$$

and the total energy is

$$E_{\text{total}}^{\text{RHF}} = E_e^{\text{RHF}} + E_N$$

Self-Consistent Field (SCF) Procedure

There is one complication with the solution of the matrix RHF equations, the Fock matrix elements depend on the solutions to the equations through the density matrix, $D_{\sigma\rho}$. To address this problem, the equations are solved iteratively:

1. Specify the molecule and geometry: nuclear coordinates, $\{R_I\}$; nuclear charges, $\{Z_I\}$; and number of electrons (N_e).
2. Select the basis set, $\{\chi_\mu\}$.
3. Calculate the integrals: $T_{\mu\nu}$, $V_{\mu\nu}^{nucl}$, $[\mu\nu|\sigma\rho]$ and $S_{\mu\nu}$.
4. Construct a guess for the density matrix, $D_{\sigma\rho}^{old}$, or expansion coefficients, $\{c_{vi}^{old}\}$.
5. Construct the Fock matrix.
6. Solve the matrix RHF equations, obtaining a new set of coefficients, $\{c_{vi}^{new}\}$.
7. Form a new density matrix $D_{\sigma\rho}^{new}$.
8. Determine if the difference between the new and old density, $|D_{\sigma\rho}^{new} - D_{\sigma\rho}^{old}|$, matrix is below a set threshold. If not, return to step #5.
9. Calculate the total energy of the molecule at the given geometry.

Selection of Basis Functions

We will now consider the selection of the functions to be used in basis sets for solving the RHF equations for atoms and molecules.

There are two important criteria for selecting these functions.

1. The functions must be capable of providing an accurate description of the atomic and molecular RHF wave functions.
2. It must be possible to rapidly calculate the integrals $T_{\mu\nu}$, $V_{\mu\nu}^{nucl}$, $[\mu\nu|\sigma\rho]$ and $S_{\mu\nu}$ with the functions.

In addition, we want the basis sets to be as compact as possible.

Hydrogenic Orbitals and Slater Functions

The solutions of the electronic Schrödinger equation for the hydrogen atom are:

$n = 1$

$$\phi_{1s} = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$$

$n = 2$

$$\phi_{2s} = \frac{1}{4} \sqrt{\frac{Z^3}{2\pi}} (2 - Zr) e^{-\frac{1}{2}Zr} \quad \phi_{2p_x} = \frac{1}{4} \sqrt{\frac{Z^3}{2\pi}} Zx e^{-\frac{1}{2}Zr}$$

etc. There are natural functions to use in the solution of the electronic Schrödinger equation. In 1930, John C. Slater proposed a slight modification of the radial functions in the hydrogenic orbitals, namely

$$r^{n-1} e^{-\zeta r}$$

Slater functions have been used extensively in calculations on atomic and diatomic molecules and, if the exponents (ζ) are optimized, have been shown to yield very accurate solutions of the HF equations. Unfortunately, it is very difficult to compute the multi-center, two-electron integrals, $[\mu\nu|\sigma\rho]$, with Slater functions. As a result, it is not feasible to use Slater functions in calculations on polyatomic molecules.

Gaussian Functions

In 1950, S. F. Boys noted that all of the integrals, including the troublesome multicenter, two-electron integrals could be computed analytically if Gaussian functions

$$\chi_{nlm\zeta}(x, y, z) = N_{nlm\zeta} x^l y^m z^n e^{-\zeta r^2}$$

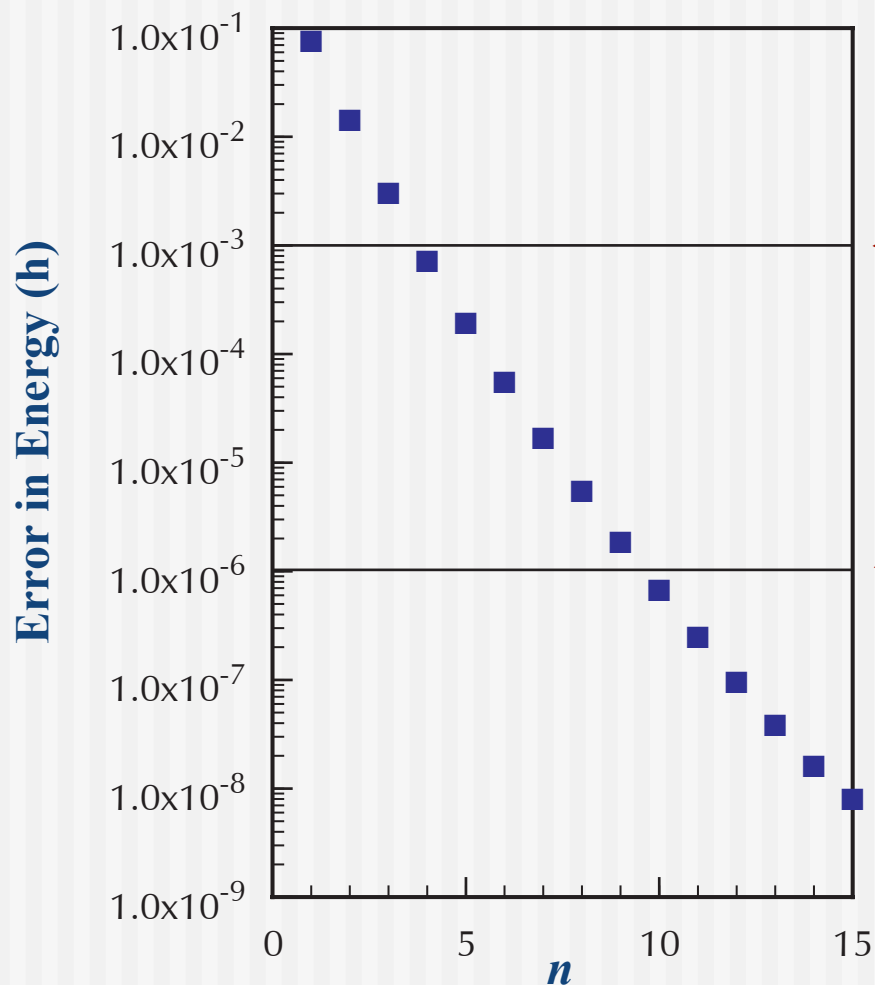
were used instead of Slater functions ($N_{nlm\zeta}$ is a normalization constant).

The occurrence of r^2 in the exponential, rather than r , causes Gaussian functions to be less appropriate than Slater functions for use in atomic and molecular calculations.

1. Mathematically, it can be shown that the wave function should have a cusp at the nucleus (origin). The derivative of the Gaussian function is continuous (and zero). So, Gaussian functions will have difficulty describing the wave function near the nucleus.
2. Mathematically, it can also be shown that, at large distances from the nucleus, the wave function should fall off exponentially with r . So, Gaussian functions will have difficulty describing the “tail” of the wave function.

Gaussian Functions and the Hydrogen Atom

To better understand how Gaussian functions may fare in atomic and molecular calculations, consider their use in the hydrogen atom.



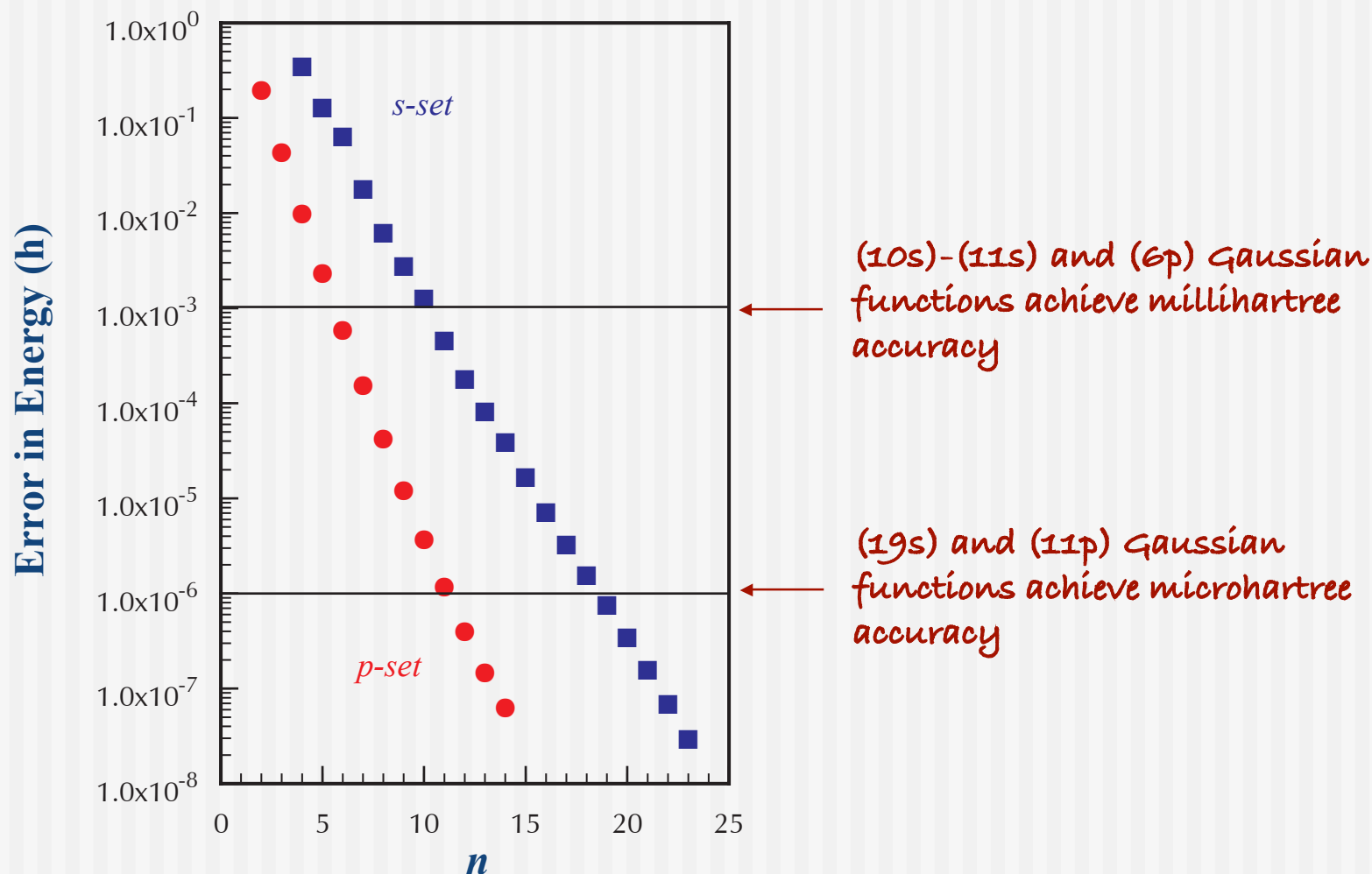
Four Gaussian functions
achieve millihartree accuracy

Ten Gaussian functions
achieve microhartree accuracy

**Not great, but not
prohibitive!**

Gaussian Functions and the Neon Atom

Let us now examine the somewhat more difficult case of the neon atom. More functions are required to achieve comparable accuracy in this case.



Gaussian Basis Sets

Much work has been done on determining the optimum Gaussian basis sets to use in molecular HF calculations. This has resulted in a proliferation of “recommended” basis sets. Many of these basis sets have been collected in the Gaussian Basis Set Library at Pacific Northwest National Laboratory:

<http://www.emsl.pnl.gov/forms/basisform.html>

In 2001, F. Jensen (*Ref. 1*) reported a systematic study of Gaussian basis sets for use in molecular HF calculations. These studies defined a sequence of basis sets that systematically approach the complete basis set limit.

To provide an accurate solution of the molecular HF equations, the basis sets must first and foremost provide an accurate description of the atomic HF orbitals. But, when a molecule is formed from atoms, the atomic orbitals are perturbed. The orbitals may contract or expand. They may become polarized toward or away from the neighboring atoms. They may even delocalize onto nearby atoms. The basis set must be able to describe all of these effects.

Augmentation of Gaussian Basis Sets

Contraction/Expansion of the Atomic Orbitals

If several Gaussian functions are used to describe an atomic orbital, most of the contraction or expansion of the orbital can be accounted for by simply varying the coefficients in the basis function expansion. Thus, expansion and contraction can be accounted for except for the smallest atomic basis sets.

Polarization of the Atomic Orbitals

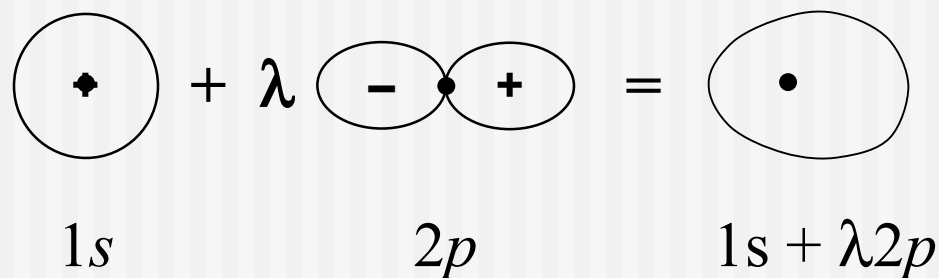
To describe polarization effects, additional functions must be added to the basis set. We will discuss this topic next.

Delocalization of the Orbitals

Delocalization of the atomic orbitals is equivalent to building ionic character into the wave function. If there is extensive delocalization, extra functions may be needed to describe the ionic character of the wave function. We will discuss this topic after we discuss polarization functions.

Polarization Functions for Gaussian Basis Sets

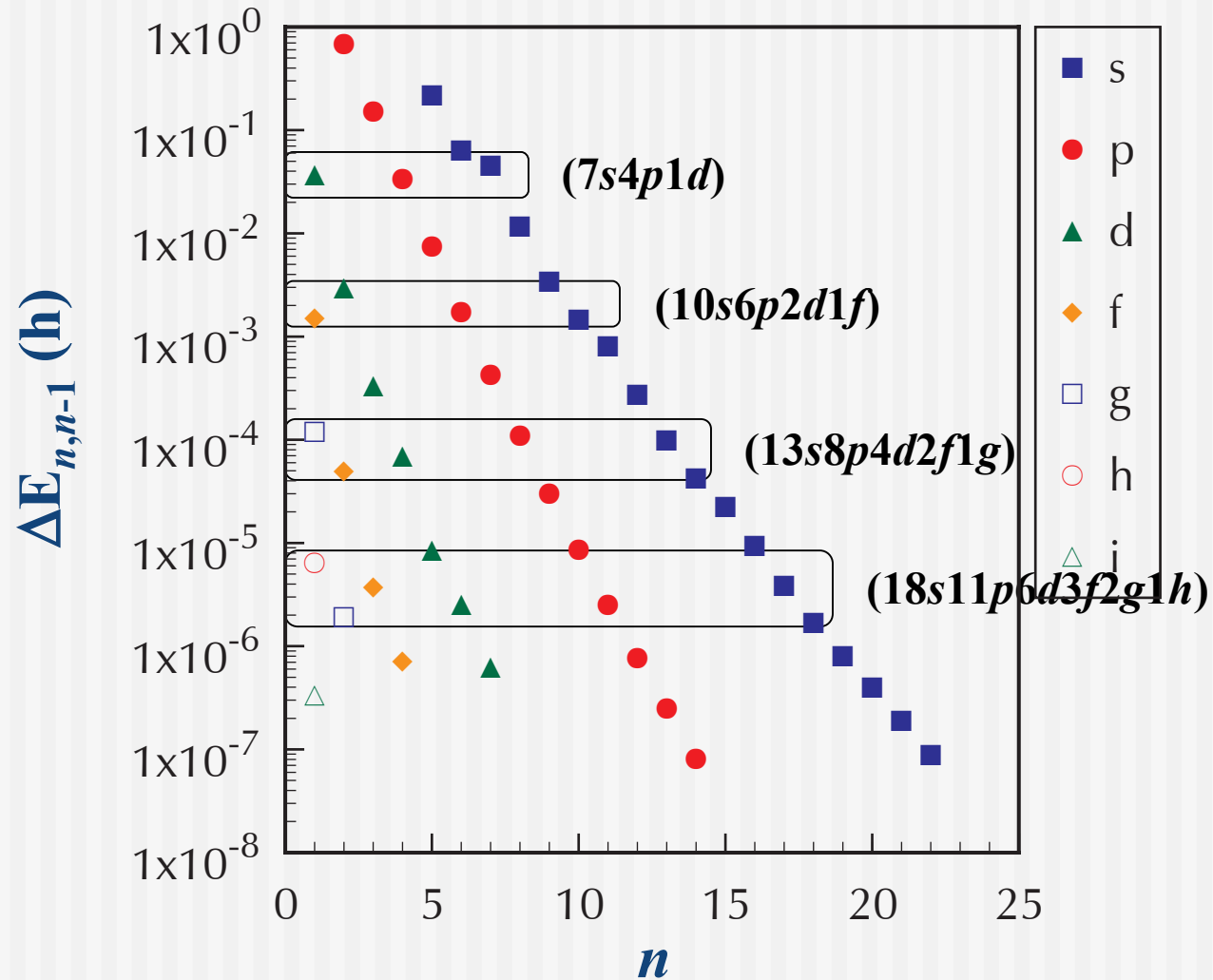
When a molecule like H_2 is formed, each of the atomic orbitals, in this case a $1s$ -orbital at $R = \infty$, polarizes toward the other atom to help strengthen the bond. It does this by mixing $2p$ character into the wave function.



So, polarizing the atomic orbitals requires the addition of higher angular momentum functions to the basis set.

Jensen (*Ref. 1*) also systematically investigated the polarization functions to include in the basis sets. He did this through calculations on a set of prototypical molecules. The (sp) and polarization sets ($dfg\dots$) were matched by requiring that the sets give rise to identical errors (to the extent that it was possible to do so).

Energy Lowerings in HF Calculations on N₂



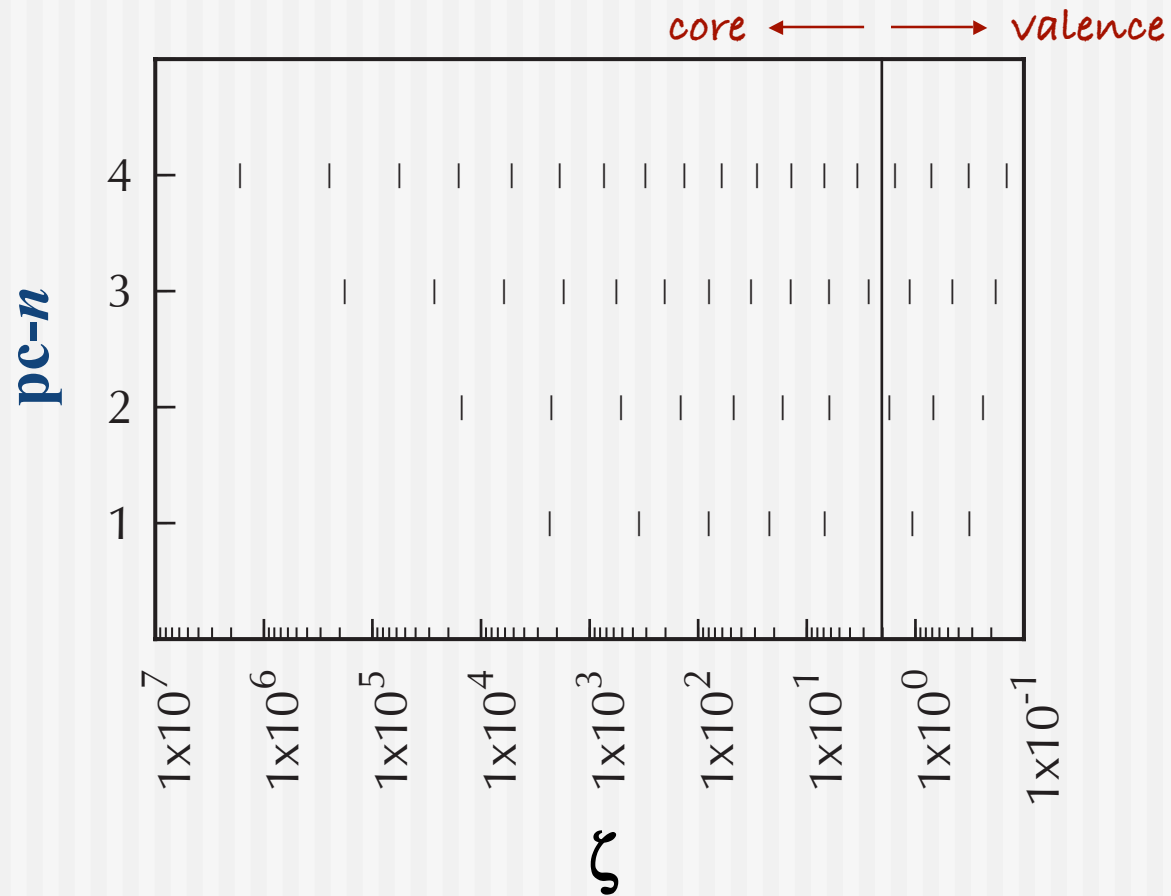
Polarization Consistent Basis Sets

Based on convergence studies of a number of prototypical molecules, Jensen proposed the following Gaussian basis sets for use in molecular calculations:

Set	H	C–F
pc-0	(3s)	(5s3p)
pc-1	(4s1p)	(7s4p1d)
pc-2	(6s2p1d)	(10s6p2d1f)
pc-3	(9s4p2d1f)	(14s9p4d2f1g)
pc-4	(11s6p3d2f1g)	(18s11p6d3f2g1h)

These sets are referred to as *polarization consistent basis sets* (pc-*n*).

pc-n Sets: Oxygen s-Exponents



Convergence of NH Properties with pc-*n* Sets

	D_e	R_e	μ_e
HF Limit ^a	48.73	1.01731	1.6133
Error^b			
(7s4p1d)	2.82	5.51	0.0844
(10s6p2d1f)	0.54	0.55	0.0636
(14s9p4d2f1g)	0.038	0.007	0.0082
(18s11p6d3f2g1h)	0.003	0.000	0.0006

^a J. Kobus, private communication.

^b In kcal/mol, milliÅ, and Debyes.

Convergence of CO Properties with pc-*n* Sets

	D_e	R_e	μ_e
HF Limit ^a	183.79	1.10178	0.2650
Error^b			
(7s4p1d)	4.71	4.09	0.0333
(10s6p2d1f)	0.852	0.46	0.0244
(14s9p4d2f1g)	0.060	0.067	0.0021
(18s11p6d3f2g1h)	0.0006	0.014	0.0003

^a J. Kobus, private communication.

^b In kcal/mol, milliÅ, and Debyes.

Diffuse Functions for Gaussian Basis Sets

In 2002, Jensen (*Ref. 3*) explored the addition of diffuse functions to the $pc-n$ sets developed for density functional (DF) calculations. Because of the similarity between DF and HF basis sets, these functions can also be used to supplement the HF basis sets also.

Addition of diffuse functions to the $pc-n$ basis sets were shown to significantly improve the convergence of a number of molecular properties such as the dipole and quadrupole moments and dipole polarizabilities as well as electron affinities. The largest improvements were realized by adding a single diffuse function to the lower angular momentum sets (s , p , and d).

Contraction of Gaussian Basis Sets

Many of the steps in HF calculations depend on the number of functions in the basis set. The size of the basis set can be reduced by combining the *primitive* basis functions (χ_p^{prim}) into *contracted* basis functions (χ_p^{cont}):

$$\chi_\mu^{cont} = \sum_{p=1}^L \chi_p^{prim} d_{p\mu}$$

Although this does not reduce the amount of work required to compute the integrals, it does reduce the work needed to diagonalize the Fock matrix.

One way to contract the basis set is to take the expansion coefficient, $\{d_{p\mu}\}$, from the atomic orbitals. This defines a minimum basis set of contracted functions. Unfortunately, such a restricted set of contracted functions cannot describe the impact of molecular formation on the atomic orbitals.

A very effective way to include these effects is to add the most diffuse primitive functions in the basis set to the minimal basis set. These are the functions that overlap the nearby atoms and provide the flexibility needed to describe the perturbations due to molecular formation.

Contracted pc-2 Set for Oxygen Atom: [4s3p]

	ζ_s	$\chi_1(1s)$	$\chi_2(2s)$	χ_3	χ_4
[4s]	14989.10	0.000522	-0.000118	0.0	0.0
	2248.08	0.004038	-0.000920	0.0	0.0
	511.616	0.020725	-0.004746	0.0	0.0
	144.713	0.080526	-0.019065	0.0	0.0
	46.9056	0.232576	-0.058999	0.0	0.0
	16.6009	0.433056	-0.137038	0.0	0.0
	6.16341	0.347467	-0.174532	0.0	0.0
	1.72634	0.041790	0.167974	0.0	0.0
	0.679615	-0.008217	0.603102	1.0	0.0
	0.236456	0.002398	0.372481	0.0	1.0
[3p]	ζ_p	$\chi_1(2p)$	χ_2	χ_3	
	62.0205	0.006269	0.0	0.0	
	14.3226	0.043187	0.0	0.0	
	4.35340	0.165515	0.0	0.0	
	1.49260	0.361422	0.0	0.0	
	0.516428	0.447563	1.0	0.0	
0.170182	0.235753	0.0	1.0		

Contracted pc-2 Set for Oxygen Atom: [2d1f]

$$\begin{array}{l} [2d] \left[\begin{array}{ccc} \zeta_d & \chi_1 & \chi_2 \\ 2.3 & 1.0 & 0.0 \\ 0.65 & 0.0 & 1.0 \end{array} \right. \\ \\ [1f] \left[\begin{array}{cc} \zeta_f & \chi_1 \\ 1.2 & 1.0 \end{array} \right. \end{array}$$

The above basis set is referred to as a *generally contracted basis set* because a primitive function can appear in any number of contracted functions, *e.g.*, the primitive *s* functions contribute to at least two contracted functions, χ_1 and χ_2 . If a primitive function appears in only one contracted function, the set is referred to as a *segmented contracted basis set*.

Generally contracted sets are more efficient than segmented contracted sets for molecular calculations. Nonetheless, most of the sets in the literature are segmented sets because most integral programs cannot efficiently handle generally contracted sets.

Contracted pc-*n* Gaussian Basis Sets

Based on studies of a number of molecules, Jensen (*Ref. 1*) proposed the following *contracted* Gaussian basis sets for use in molecular calculations:

Set	H	C–F
pc-0	[2 <i>s</i>]	[3 <i>s</i> 2 <i>p</i>]
pc-1	[2 <i>s</i> 1 <i>p</i>]	[3 <i>s</i> 2 <i>p</i> 1 <i>d</i>]
pc-2	[3 <i>s</i> 2 <i>p</i> 1 <i>d</i>]	[4 <i>s</i> 3 <i>p</i> 2 <i>d</i> 1 <i>f</i>]
pc-3	[5 <i>s</i> 4 <i>p</i> 2 <i>d</i> 1 <i>f</i>]	[6 <i>s</i> 5 <i>p</i> 4 <i>d</i> 2 <i>f</i> 1 <i>g</i>]
pc-4	[7 <i>s</i> 6 <i>p</i> 3 <i>d</i> 2 <i>f</i> 1 <i>g</i>]	[8 <i>s</i> 7 <i>p</i> 6 <i>d</i> 3 <i>f</i> 2 <i>g</i> 1 <i>h</i>]

Convergence of NH Properties with pc-*n* Sets

	D_e	R_e	μ_e
HF Limit ^a	48.73	1.01731	1.6133
Error^b			
[3s2p1d]	3.77	10.78	0.0560
[4s3p2d1f]	0.612	0.58	0.0651
[6s5p4d2f1g]	0.046	0.008	0.0082
[8s7p6d3f2g1h]	0.003	0.000	0.0006

^a J. Kobus, private communication.

^b In kcal/mol, milliÅ, and Debyes.

References

1. “Polarization consistent basis sets: Principles,” F. Jensen, *J. Chem. Phys.* **115**, 9113-9125 (2001).
2. “Polarization consistent basis sets. II. Estimating the Kohn-Sham basis set limit,” F. Jensen, *J. Chem. Phys.* **116**, 7372-7379 (2002),
3. “Polarization consistent basis sets. III. The importance of diffuse functions,” F. Jensen, *J. Chem. Phys.* **117**, 9234-9240 (2002).
4. “Polarization consistent basis sets. IV. The basis set convergence of equilibrium geometries, harmonic vibrational frequencies, and intensities,” F. Jensen, *J. Chem. Phys.* **118**, 2459-2463 (2003).
5. “Polarization consistent basis sets. V. The elements Si-Cl,” F. Jensen, *J. Chem. Phys.* **121**, 3463-3470 (2004).