Quantum Theory of Molecular Electronic Structure

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Quantum mechanics

- Historical viewpoints

*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*

P. A. M. Dirac
Quantum mechanics

- Historical viewpoints

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

P. A. M. Dirac

Nobody understands quantum mechanics.

R. P. Feynman
Quantum mechanics


- Uncertainty principle: $\Delta p \Delta x \geq \hbar$.

- Einstein didn’t like it; various “interpretations”.

- Schrödinger’s cat. Tunnelling phenomena ($\alpha$-decay). Hidden variables.

- Difference between physicists and chemists.
Quantum mechanics

- Set of assumptions governing the dynamics of a subset of fundamental particles.

- Part physics, part maths, part philosophy.

- We shall ignore all the philosophy, and most of the maths.

- However, a serious study of quantum chemistry inevitably requires some mathematics.

- No derivations: proof by assertion.
The Schrödinger Equation

- Wave mechanical equation

\[ H(\tau_1, \tau_2 \ldots \tau_N) \Psi(\tau_1, \tau_2 \ldots \tau_N) = E \Psi(\tau_1, \tau_2 \ldots \tau_N), \]

\( E \) is the total energy, \( \Psi \) is the wave function, and \( H \) is the Hamiltonian operator. \( \tau_i \) is the coordinates of the \( i \)th particle.

- Classically, \( H = T + V \), kinetic and potential energy, respectively.

- \( \Psi \) contains all the information about the system.
The Wave Function

- Since all the particles have to be somewhere, we have the normalization condition

\[ \int \Psi(\tau_1, \tau_2 \ldots \tau_N)^* \Psi(\tau_1, \tau_2 \ldots \tau_N) d\tau_1 d\tau_2 \ldots d\tau_N = 1. \]

- Probabilistic interpretation: \( \Psi(\tau_1, \tau_2 \ldots \tau_N)^* \Psi(\tau_1, \tau_2 \ldots \tau_N) \) gives the probability of finding the system with particle 1 at \( \tau_1 \), etc.
Hamiltonian operator

- Kinetic energy: classically given as

\[ T = \frac{1}{2}mv^2 = \frac{1}{2m}p^2, \]

since \( p = mv \).

- Quantum mechanically, \( p = -i\hbar \nabla \), so

\[ T = -\frac{1}{2m}\nabla^2 = -\frac{1}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right), \]

where we have used atomic units: \( \hbar = m_e = e = 1 \).

- Hence \( H = -(1/2m)\nabla^2 + V \).

- Consider the hydrogen atom: one electron and one fixed proton, Coulomb \((1/r)\) potential.
The hydrogen atom

- \( V = 1/r \). \( T = -\frac{1}{2m} \nabla^2 \). \( T \) expressed in terms of Cartesians, \( V \) in terms of the internal scalar distance

\[ r = \left( x^2 + y^2 + z^2 \right)^{\frac{1}{2}}. \]

- From the symmetry of the system (spherically symmetric potential) we are better off using spherical coordinates \((r, \theta, \phi)\).

- \( \Psi \) then factorizes into radial and angular parts.
Angular Wave Function

• The angular part is a spherical harmonic, $Y_{lm}(\theta, \phi)$ like $s = Y_{00}$, $p_z = Y_{10}$, $d_{xz} = Y_{21}$ etc. Orthonormality:

$$\int \int Y_{lm}(\theta, \phi)^* Y_{pq}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{lp} \delta_{mq}$$
Angular Wave Function
Angular Wave Function

defaults used

Edge = 3.00 Space = 0.2000 Psi = 10
Radial Wave Function

- The radial part is a polynomial in $r$ times $\exp(-\zeta r)$. Also orthonormal: $1s$, $2s$, etc.

$$\int 1s(r)^*2s(r)r^2dr = 0$$

Note cusp behaviour as $r \to 0$: cancels $1/r$ term in $H$. 
The hydrogen atom

Figure 1: H 1s radial function
The hydrogen atom

Figure 2: H $2s$ radial function
The hydrogen atom

Figure 3: H $1s$ and $2s$ radial functions
The hydrogen atom

- Exact solution (basically by a suitable choice of coordinates).
- Near-perfect agreement with experimental observations (not perfect because nonrelativistic).
- Gave enormous confidence in early days that quantum mechanics was fundamentally correct.
- So, beyond H? He, H$_2$?
The helium atom

- Two electrons, fixed nucleus:

\[ H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}. \]

- Defies analytical solution (so far — probably a Nobel prize in it, though...).

- Term in \( r_{12}^{-1} \) is nonseparable: no product of functions of electrons 1 and 2 can be the exact solution.

- The naive guess: \( 1s(1)1s(2) \), spin-paired, is not an eigenfunction of \( H \).
Variational methods

- Return to the Schrödinger equation

\[ H \Psi = E \Psi. \]

Multiplying by \( \Psi^* \) and integrating over all space gives

\[ \frac{\int \Psi^* H \Psi d\tau}{\int \Psi^* \Psi d\tau} = E. \]

Often written as

\[ \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E, \]

Dirac “bra-ket” notation.
Variational methods

- *Any* guess at the wave function (say, $\Phi$) obeys

$$\frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E,$$

the equality holding only for the exact solution (Variation Principle).

- Guess a trial wave function with some adjustable parameters, and then adjust them to minimize $\langle \Phi | H | \Phi \rangle / \langle \Phi | \Phi \rangle$. This is the *variational method*. 
The helium atom

- We know that a wave function of the form $1s^2$ is not exact, but what is our best estimate? We can imagine that the hydrogen orbitals are too diffuse, because He has a higher charge than H. This could be accommodated by increasing $\zeta$ in the radial function $\exp(\zeta r)$ to two, say: 1.7 is optimal.

- Energy is $-2.75$ atomic units, compared to an experimental value of $-2.90$ atomic units. 5%, but this error is 94 kcal/mol!
The helium atom

- A better trial function (Hylleraas) would be

\[
\exp(-\zeta[r_1 + r_2]) \sum_{nlm} c_{nlm} (r_1 + r_2)^n (r_1 - r_2)^{2l} r_{12}^m,
\]

where we see our original product of exponentials has been multiplied by polynomials in \(r_1\), \(r_2\), and \(r_{12}\). Six terms give an accuracy of 1 kcal/mol.

- But this only works for helium, or (in a modified form) \(H_2\). How do we deal with many-electron systems?
Spin and antisymmetry

- Electrons have a spin which is quantized, up or down. Particles with half-integral spins (like electrons) are fermions. Fermion wave functions are antisymmetric with respect to particle interchange:

\[ \Psi(1, 2 \ldots) = -\Psi(2, 1 \ldots). \]

- Our simple helium wave function was two 1s electrons, spin-paired. Denoting spin-down by a bar, it was \( 1s(1)\bar{1}s(2) \): neither symmetric nor antisymmetric with respect to particle interchange, which gives \( 1s(2)\bar{1}s(1) \).
Slater determinants

- The form $1s(1)\bar{1s}(2) - 1s(2)\bar{1s}(1)$ is antisymmetric. It could be written as

\[
\begin{vmatrix}
1s(1) & 1s(1) \\
1s(2) & 1s(2)
\end{vmatrix}.
\]

Normalized by $2^{-\frac{1}{2}}$, this is termed a Slater determinant. Often represented by the diagonal alone:

\[
\begin{vmatrix}
1s(1)1s(2)
\end{vmatrix}.
\]

- The great advantage of the Slater determinant is that it can be generalized to any number of electrons.
Slater determinants

- Consider three electrons in three arbitrary orbitals $a, b, c$. The Slater determinant

$$|a(1)b(2)c(3)|$$

can be expanded as

$$\frac{1}{\sqrt{3!}} \left\{ a(1)b(2)c(3) - a(1)b(3)c(3) - a(2)b(1)c(3) 
+ a(2)b(3)c(1) + a(3)b(1)c(2) - a(3)b(2)c(1) \right\}.$$  

- Note the compact notation: $N!$ terms represented in an $N \times N$ array, or just as the elements of the diagonal.
The Born-Oppenheimer Approximation

- The Hamiltonian for several nuclei and electrons would be

\[ H = - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{A>B} \frac{Z_AZ_B}{r_{AB}}, \]

where \( A \) runs over nuclei, \( i \) over electrons. Note that unlike an atom in free space we now have a term in nuclear motion. Wave function would be \( \Psi(r_i, r_A) \).

- Nuclei are *much* heavier than electrons (at least 2000 times). *Decouple* problem: assert that there is no coupling between electronic motion (fast) and nuclear motion (slow).
The Born-Oppenheimer Approximation

- Write wave function as $\Psi(r_i; R_A)$, where we have a different electronic wave function for each value of the parameters $R_A$ — coordinates of fixed nuclei.

Eigenfunction of

$$
H = - \sum_i \frac{1}{2} \nabla_i^2 r_i - \sum_A \sum_i \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}}.
$$
The Born-Oppenheimer Approximation

- Electronic Schrödinger equation

\[ H(r_i; R_A)\Psi(r_i; R_A) = E(R_A)\Psi(r_i; R_A), \]

the function \( E(R_A) \) defines the potential energy surface for nuclear motion.

- Get rotational and vibrational energy levels for the nuclear part of the problem, by solving

\[ \left\{ -\sum_A \frac{1}{2M_A} \nabla^2_A + E(R_A) \right\} \Phi(R_A) = E_{\text{nuc}} \Phi(R_A), \]

where \( \Phi(R_A) \) is the nuclear motion wave function. Also determines chemical dynamics.
The Born-Oppenheimer Approximation

- Note that this is an approximation — properly speaking there are just eigenvalues of the full Hamiltonian, representing “rovibronic” levels. But a very good one.

- Fixing the nuclei has a drastic effect on the symmetry of the system! The symmetry is determined by the static nuclear framework.
Hartree-Fock theory

- Even with the Born-Oppenheimer approximation, we can make no progress on analytical solution of the Schrödinger equation.

- Start simple: assume traditional molecular orbital ideas hold. For a system of $2N$ electrons, assume that the wave function is given by allocating electrons in pairs to molecular orbitals $\psi$.

- Physically, as we shall see, this is like assuming that the electrons interact only with the average potential of all the other electrons. Independent-particle model, or mean-field theory.
Hartree-Fock theory

- Assume that the MOs are orthonormal (and here real)

\[ \int \psi_i(r_1) \psi_j(r_1) dr_1 = \delta_{ij}. \]

- Trial wave function is a Slater determinant

\[ \left| \psi_1(r_1) \bar{\psi}_1(r_2) \psi_2(r_3) \bar{\psi}_2(r_4) \cdots \psi_N(r_{2N-1}) \bar{\psi}_N(r_{2N}) \right|. \]

Substitute into the variation principle, and make stationary with respect to the form of the MOs.
Hartree-Fock Theory

- Need to evaluate $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ for this form of $\Psi$. Helped here by the orthonormality of the MOs, and by the form of $H$.

- $H$ contains zero-, one- and two-electron operators only. In the integral over all space, we have contributions from the coordinates of $N - 2$ electrons that are just products of integrals

$$\int \psi_i(r_1) \psi_j(r_1) dr_1 = \delta_{ij},$$

so thanks to orthonormality we end up with only one- and two-electron integrals;
Hartree-Fock theory

\[
\langle \psi_1(r_1) \bar{\psi}_1(r_2) \ldots | H | \psi_1(r_1) \bar{\psi}_1(r_2) \ldots \rangle = 2 \sum_i h_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}),
\]

where

\[
h_{ij} = \int \psi_i(r_1) \left\{ -\frac{1}{2} \nabla^2 - \sum_A Z_A r_{Ai}^{-1} \right\} \psi_j(r_1) dr_1
\]

\[
J_{ij} = \int \int \psi_i(r_1) \psi_i(r_1) r_{12}^{-1} \psi_j(r_2) \psi_j(r_2) dr_1 dr_2 = (ii|jj)
\]

\[
K_{ij} = \int \int \psi_i(r_1) \psi_j(r_1) r_{12}^{-1} \psi_i(r_2) \psi_j(r_2) dr_1 dr_2 = (ij|ij)
\]
The Hartree-Fock equations

- The expression

\[ 2 \sum_i h_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) \]

is the energy for a given guess at the MOs. We optimize the MOs by minimizing this energy (variational method).

- Minimizing the energy requires satisfying the Hartree-Fock equations

\[ F_{ij} = \epsilon_i \delta_{ij}, \]

where \( \epsilon_i \) is termed the orbital energy of orbital \( \psi_i \), and

\[ F_{ij} = h_{ij} + \sum_k \left[ 2(ij|kk) - (ik|jk) \right], \]

is the Fock operator.
The Hartree-Fock equations

- *Note the sum over all occupied orbitals here.* The solutions depend on themselves! This is not a simple eigenvalue problem.

- *Self-consistent field (SCF) approach:* guess a set of MOs, construct $\mathbf{F}$, diagonalize, and use its eigenvectors as a (hopefully) better guess at the MOs.
Solving the SCF equations

- For atoms, the symmetry of the system factors the SCF equations into an angular part (spherical harmonics again!) and a radial part. The radial equations can be solved numerically (one-dimensional problem).

- For molecules, the lower symmetry does not permit any factorization in general. Numerical methods have been used for diatomic molecules, but becomes expensive and cumbersome for polyatomic systems.

- How do we then express the MOs? Expand them in a fixed basis set, just like the traditional LCAO (linear combination of atomic orbitals) reasoning used in qualitative MO theory.
The SCF equations

- Let us expand the unknown MOs linearly in a set of basis functions

\[ \psi_i = \sum_{\mu} \chi_{\mu} C_{\mu i} . \]

Here \( \chi_{\mu} \) can be any functions deemed appropriate. They are often approximations to atomic orbitals on the individual centres, and are often termed “atomic orbitals” (AOs).

- Note that the AOs are not required to be orthonormal:

\[ \int \chi_{\mu}(r_1)\chi_{\nu}(r_1)dr_1 = S_{\mu \nu} \neq \delta_{\mu \nu} . \]
The SCF equations

- The SCF equations now become

\[ \sum_{\nu} F_{\mu \nu} C_{\nu i} = \sum_{\nu} S_{\mu \nu} C_{\nu i} \epsilon_i, \]

where

\[ F_{\mu \nu} = h_{\mu \nu} + \sum_{\lambda \sigma} D_{\lambda \sigma} \mathcal{P} (\mu \nu | \lambda \sigma), \]

\[ D_{\lambda \sigma} = 2 \sum_{i} C_{\lambda i} C_{\sigma i}, \]

\[ \mathcal{P} (\mu \nu | \lambda \sigma) = (\mu \nu | \lambda \sigma) - \frac{1}{4} (\mu \lambda | \nu \sigma) - \frac{1}{4} (\mu \sigma | \nu \lambda). \]
SCF Calculations

- Choose a basis $\chi_\mu$.
- Calculate the integrals over this basis (store on disk).
- Guess the MO coefficients $C$.
- Construct $D$, then $F$. Solve the equations for a new $C$. If it does not agree with the previous estimate, iterate until it does.
The LCAO SCF method

- This approach of writing the unknown molecular orbitals in terms of a fixed basis $\chi$ is known as the \emph{linear combination of atomic orbitals} (LCAO) approach.

- Classic qualitative approach to molecular orbital theory.

- Originally introduced with the idea of using atomic orbitals as the basis, but this creates problems.

- To form $\mathbf{F}$, we \textit{must} be able to compute the integrals over the one- and two-electron operators in the Hamiltonian

$$h_{\mu\nu} = \int \chi_\mu(r_1) \left( -\frac{1}{2} \nabla^2 - \sum_A Z_A r_A^{-1} \right) \chi_\nu(r_1) dr_1$$

$$\langle \mu\nu | \lambda\sigma \rangle = \int \int \chi_\mu(r_1) \chi_\nu(r_1) r_{12}^{-1} \chi_\lambda(r_2) \chi_\sigma(r_2) dr_1 dr_2.$$
Basis functions

- Similar qualitative reasoning as H atom: exponential behaviour near nucleus, and exponential decay at long range.

- So use

\[ \exp(-\zeta r_A) r_A^l Y_{lm}(\theta_A, \phi_A), \]

a *Slater-type orbital* (STO) centred on nucleus \( A \).

- Works nicely for atoms (one-centre integrals); works for diatomic molecules (two-centre integrals) but requires some numerical integration.

- Works for linear polyatomics, but integral expressions are very difficult and numerical integration is required in a number of cases.

- No algorithm for nonlinear molecules. None.
Other choices of basis functions

- Boys suggested *Gaussian-type orbitals* (GTO)

\[
\exp(-\alpha r_A^2) r_A^l Y_{lm}(\theta_A, \phi_A)
\]

or the “Cartesian” form

\[
x_A^l y_A^m z_A^n \exp(-\alpha r_A^2),
\]

which are closely related.

- Multicentre integrals are all easy (relatively speaking). Require at most a one-dimensional numerical integration, by quadrature.

- What about the physics?
STOs vs GTOs

Figure 4: Unit exponent normalized GTO and STO

Solid line: GTO; Dashed line: STO
The hydrogen atom

Figure 5: Optimum GTO for H 1s

Solid line: GTO; Dashed line: STO
The hydrogen atom

- What about using more than one GTO?

Figure 6: Four-term GTO expansion for H 1s

Solid line: GTO; Dashed line: STO
GTO basis sets

- Cannot solve H exactly with finite expansion in GTOs (needs only one STO!).

- Combination of several GTOs much better — need bigger GTO basis sets than STO sets.

- Some GTO sets combine a few GTOs together into one basis function before we start (contracted basis functions).

- Perform quite well: virtually all electronic structure calculations use Gaussians.
LCAO SCF

- Clearly, the number of basis functions $M$ we use must be at least as large as the number of occupied orbitals $N$.

- If $M > N$, in addition to the $N$ occupied orbitals, the SCF procedure will generate $M - N$ virtual (i.e., unoccupied) MOs.

- Koopmans’ Theorem: the orbital energies $\epsilon_i$ of the occupied orbitals correspond to ionization potentials; the orbital energies $\epsilon_a$ of any virtual orbitals correspond to electron affinities. These are the best estimates we can get (variationally) without reoptimizing the MOs for the ion state.

- Does not hold for excitation energies: $\epsilon_a - \epsilon_i$ is not the best estimate of the energy for exciting from orbital $i$ to $a$. 
Open-shell SCF

- Ions take us in the direction of *open-shell* systems: most generally, systems with unpaired electrons. E.g., H$_2$O$^+$, O$_2$.

- Want to extend our closed-shell Hartree-Fock method to open shells.

- Simplest approach is not to worry about pairing electrons up in orbitals at all:

\[
\Psi = |\psi_1(r_1)\psi_2(r_2)\ldots|,
\]

where each *spin-orbital* $\psi_i$ may have $\alpha$ or $\beta$ spin.
Open-shell SCF

• E.g., Li atom

\[
\left| \psi_1(r_1) \bar{\psi}_2(r_2) \psi_3(r_3) \right| ,
\]

where presumably \( \psi_1 \) and \( \psi_2 \) will look like a 1s orbital and \( \psi_3 \) like a 2s.

• Recall that spin-orbitals of different spin are orthogonal anyway: there is no requirement here that \( \psi_1 \) and \( \psi_2 \) have the same space part.
Unrestricted Hartree-Fock theory

- Since the terms in the Hamiltonian operator have no spin dependence, there can be no terms in the energy involving orbitals of different spin (e.g., no $h_{ii}$).

- Fock operator (and the rest of the matrices) block into two parts, one for $\alpha$ spin-orbitals and one for $\beta$:

$$ F^\alpha_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} \left\{ \left[ D^\alpha_{\lambda\sigma} + D^\beta_{\lambda\sigma} \right] (\mu\nu|\lambda\sigma) - D^\alpha_{\lambda\sigma} (\mu\lambda|\nu\sigma) \right\}, $$

$$ F^\beta_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} \left\{ \left[ D^\alpha_{\lambda\sigma} + D^\beta_{\lambda\sigma} \right] (\mu\nu|\lambda\sigma) - D^\beta_{\lambda\sigma} (\mu\lambda|\nu\sigma) \right\}, $$

where

$$ D^\alpha_{\lambda\sigma} = \sum_i C^\alpha_{\lambda i} C^\alpha_{\sigma i}. $$
Unrestricted Hartree-Fock theory

- The disadvantage of this approach is that no restrictions are applied to retain symmetry properties of the wave function. Comes out contaminated with other spin states. But it’s cheap.
Restricted Hartree-Fock Theory

- What’s wrong with (what seems to be) the simple idea of using, e.g.,

\[ |\psi_1\psi_1\psi_2\psi_2\cdots\psi_N\psi_N\psi_{N+1}\psi_{N+2}\cdots|, \]

the naive open-shell extension to a closed-shell determinant? This is called restricted Hartree-Fock.

- The closed-shell determinant is invariant to mixing the occupied orbitals among themselves. Or any virtuals among themselves, but not occupieds with virtuals.

- So is the unrestricted Hartree-Fock determinant.
Restricted Hartree-Fock Theory

- But the restricted case is not invariant to mixing occupieds among themselves! Because the spin-orbitals $\overline{\psi}_{N+1}, \overline{\psi}_{N+2} \ldots$ do not appear, and if they are mixed into the other $\beta$ spin-orbitals they will change the wave function.

- This makes the optimization of the energy much harder: have to account for mixing between doubly and singly occupied MOs. But there is no spin contamination in the wave function.
Basis sets

- In the earliest days people hoped to get away with a single STO for each AO occupied in the atoms forming the molecule. E.g., $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ for B–Ne.

- Such a *minimal* or single-zeta (SZ) basis does not work well, because it is not flexible enough to describe how the atomic orbitals deform in the molecule.

- Next step, use two STOs to describe each orbital: *double-zeta* (DZ) basis. Or even more (triple-zeta, etc.).

- Molecules are lower symmetry than atoms — orbitals empty in the atoms can contribute, like $d$ functions in first-row molecules, or $p$ functions on hydrogen! *Polarization* functions — DZP basis, etc.
GTO basis sets

- For present purposes, we can assume that the STO designations can be used to identify basis sets of the same quality as the STO sets.

- Thus an SZ set is not one GTO per AO (which would be useless), but enough GTOs to describe each AO as well as one STO, etc.

- Vast number of basis sets of varying quality. Basis sets that give good energies and structures do not always give good properties.
GTO basis sets

- Common sets: STO-3G (an SZ set), 4-31G, 6-31G (both DZ valence). From GAUSSIAN. Then DZ or DZP (Dunning), and larger sets (TZP or TZ2P) etc.

- Polarization functions are very important (even though they increase the expense) — NH$_3$ is planar without $d$ functions!
SCF results for $\text{H}_2\text{O}$

- Study convergence of energy, structure and harmonic frequencies with basis set.
- Hartree-Fock limit results from aug-cc-pVQZ-\(g\) set.
- Minimal basis set: STO-3G — $(6s \ 3p)$ contracted to $[2s \ 1p]$ for O based on fit of three GTO to one STO. Results poor.
- Small $sp$ sets: 4-31G and 6-31G — $[3s \ 2p]$ contraction of $(8s \ 4p)$ and $(10s \ 4p)$, respectively, *split-valence* or valence double zeta (VDZ). Results fair.
- Other DZ or VDZ sets, e.g., those based on $(9s \ 5p)$. Results similar to VDZ.
### SCF results for H$_2$O

<table>
<thead>
<tr>
<th>Basis</th>
<th>$E_{\text{SCF}}$ $\left( E_h \right)$</th>
<th>$r_e$ (Å)</th>
<th>$\angle \text{HOH}$ (°)</th>
<th>$\omega_1$ (cm$^{-1}$)</th>
<th>$\omega_2$ (cm$^{-1}$)</th>
<th>$\omega_3$ (cm$^{-1}$)</th>
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</table>
SCF results for H$_2$O

- Need polarization functions for improved results: $d$ set on O and $p$ set on H, etc.

- Even the smallest polarized basis results are now in good agreement with the largest set.

- Need polarization functions on all atoms: 6-31G** set much better than 6-31G* (latter has only $d$ on O).

- Conclude that for structures and frequencies a DZP basis is rather close to the best Hartree-Fock result. What causes the remaining errors?
Breakdown of the Hartree-Fock model

- Consider the molecule H\(_2\). As the bond length increases, the wave function goes to a product \(1s_A \ 1s_B\) of the H atom wave functions on centres \(A\) and \(B\). Antisymmetrizing and pairing up the spins gives

\[
\Psi_{\text{exact}} = \frac{1}{\sqrt{2}} \left\{ |1s_A \ 1s_B| - |1s_A \ 1s_B| \right\}.
\]

- The Hartree-Fock wave function for H\(_2\) is just

\[
\Psi_{\text{HF}} = |\sigma_g \ \bar{\sigma}_g|,
\]

where

\[
\sigma_g = \frac{1}{\sqrt{2 + 2S}} \ (1s_A + 1s_B),
\]

and

\[
S = \int 1s_A(r_1)1s_B(r_1)dr_1.
\]
Breakdown of the Hartree-Fock model

- So at long distance, where $S = 0$,

\[
\Psi_{HF} = \frac{1}{\sqrt{2}} \left( 1s_A + 1s_B \right) \frac{1}{\sqrt{2}} \left( \overline{1s_A} + \overline{1s_B} \right)
\]

\[
= \frac{1}{2} \left\{ \left| 1s_A \overline{1s_B} \right| - \left| \overline{1s_A} 1s_B \right| \right\} + \frac{1}{2} \left| 1s_A \overline{1s_A} \right| + \frac{1}{2} \left| 1s_B \overline{1s_B} \right|
\]

\[
= \frac{1}{\sqrt{2}} \Psi_{exact} + \frac{1}{2} \left| 1s_A \overline{1s_A} \right| + \frac{1}{2} \left| 1s_B \overline{1s_B} \right|.
\]
Breakdown of the Hartree-Fock Model

- So at long distances in $\text{H}_2$, Hartree-Fock does not give the product of two H atom wave functions. Rather, it gives 50% ($\text{H} + \text{H}$), and 50% ($\text{H}^+ + \text{H}^-$). “Covalent” and “ionic” terms.

- Evidently, the ionic term should disappear at long distances.

- If we proceed backwards, we discover that (at long distance)

$$
\Psi_{\text{exact}} = \frac{1}{\sqrt{2}} \left\{ |\sigma_g \overline{\sigma}_g| - |\sigma_u \overline{\sigma}_u| \right\},
$$

where

$$
\sigma_u = \frac{1}{\sqrt{2 - 2S}} (1s_A - 1s_B)
$$

is the antibonding combination of the atomic $1s$. 
Breakdown of the Hartree-Fock Model

- As the bond forms, the variation principle tells us we can only benefit from generalizing $\Psi_{HF}$ to

$$\Psi_{MCHF} = c_g |\sigma_g \bar{\sigma}_g| + c_u |\sigma_u \bar{\sigma}_u|,$$

where $c_g$ and $c_u$ can be optimized together with the MOs. This is the multiconfigurational Hartree-Fock or multiconfigurational SCF (MCSCF) method.

- At long distance, $c_g = \frac{1}{\sqrt{2}}$ and $c_u = -\frac{1}{\sqrt{2}}$, while near equilibrium we can expect $c_g \approx 1$ and $c_u \ll 1$. 
The Hartree-Fock model revisited

- We have already seen that the Hartree-Fock approach is unreliable when we are breaking even the simplest chemical bond. This is because other configurations become nearly degenerate in energy with Hartree-Fock.

- There is a more subtle problem. Hartree-Fock views each electron as interacting with a an averaged potential generated by the others. But the Hamiltonian actually contains the Coulomb repulsion between pairs of electrons $r_{ij}^{-1}$. 
The Hartree-Fock model revisited

- Our knowledge of singularities in $H$ tells us there will be cusp behaviour in the exact wave function as $r_{ij} \to 0$ that cancels this. In fact

$$\lim_{r_{ij} \to 0} \Psi = 1 + \frac{1}{2}r_{ij}. $$

So the exact wave function must involve at least terms linear in $r_{ij}$.

- The effect is that electrons will avoid each other more than the Hartree-Fock approximation would suggest. *Electron correlation*. Correlation energy

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}.$$
Electron correlation

- Obvious solution: extend the approximate wave function so that instead of just products of one-electron functions, it contains two-electron functions of $r_{ij}$ (remember Hylleraas?).

- Fine for two electrons, troublesome for three...
Electron correlation

- Make more use of the basis set. For instance, we have virtual MOs as well as occupied MOs. If $\Psi_0$ denotes the Hartree-Fock determinant

$$\Psi_0 = |\psi_1 \psi_2 \ldots \psi_i \ldots \psi_N|,$$

we can start to replace the occupied orbitals with virtual orbitals to build more configurations:

$$\Psi_i^a = |\psi_1 \psi_2 \ldots \psi_a \ldots \psi_N|,$$

$$\Psi_{ij}^{ab} = |\psi_1 \psi_2 \ldots \psi_a \ldots \psi_b \ldots \psi_N|,$$

e tc.
Configuration interaction

- The variation principle tells us that if we allow all these configurations to mix — *configuration interaction* (CI) — we will get a lower energy than Hartree-Fock: thus we are accounting for electron correlation.

\[
\Psi_{\text{CI}} = c_0 \Psi_0 + \sum_i \sum_a c_i^a \Psi_i^a + \sum_{i>j} \sum_{a>b} c_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{i>j>k} \sum_{a>b>c} c_{ijk}^{abc} \Psi_{ijk}^{abc} \ldots
\]

- We can then optimize the coefficients \( c \) by making

\[
\frac{\langle \Psi_{\text{CI}} | H | \Psi_{\text{CI}} \rangle}{\langle \Psi_{\text{CI}} | \Psi_{\text{CI}} \rangle}
\]

stationary.
Configuration interaction

- This has obvious similarities with the MCSCF approach we came up with for $H_2$. However, in CI we do not reoptimize any orbitals.

- Typically, MCSCF is used only to deal with the problem of near degeneracies, sometimes termed *nondynamical correlation*, as opposed to the *dynamical correlation* mediated by $r_{ij}^{-1}$ in $H$.

- For $M$ MOs ($N$ occupied), the number of configurations behaves as

\[
\frac{M!}{N!(M - N)!}.
\]

For Ne (10 electrons) in a DZP basis (15 basis functions) this is about 30 million terms. Not generally feasible to include all of them!
Configuration interaction

- We recall that the Hamiltonian contains only one- and two-electron operators, and that the MOs form an orthonormal set.

- Then all matrix elements

\[ \langle \Psi_0 | H | \Psi_{ijk\ldots}^{abc\ldots} \rangle = 0 \]

for three or more substitutions. Thus only the single and double excitations interact with \( \Psi_0 \).
Configuration interaction

- Restrict $\Psi_{CI}$ to only single and double excitations (CISD):

$$\Psi_{CISD} = c_0 \Psi_0 + \sum_i \sum_a c_i^a \Psi_i^a + \sum_{i>j} \sum_{a>b} c_{ij}^{ab} \Psi_{ij}^{ab}.$$ 

- This is a popular and longstanding method for calculating correlation energies. Its advantages and disadvantages will be discussed later.
Perturbation theory

- Mathematical method for dealing with an unknown or intractable system, by building on a known system.

- For example, Hartree-Fock seems to be a pretty good approximation: treat correlation by looking at the difference between the exact Hamiltonian and the Fock operator.

- Expand the exact wave function and energy in a power series about the Hartree-Fock solution: expect a convergent series of contributions from each order (term).

- Second order (denoted MP2) cheap, MP3 more expensive and less reliable, MP4 is as high as is usually practical.

- Idea works best when exact wave function strongly dominated by Hartree-Fock. Fails for significant nondynamical correlation.
CI or perturbation theory?

- CI is variational — upper bound to the exact energy. Can handle nondynamical correlation.

- Perturbation theory is **size-extensive**: scales correctly with the number of particles in the system. Sometimes “size-consistency”.

- Suppose we have $n$ He atoms a long distance apart. The total energy is clearly $nE_{He}$. True for the Hartree-Fock model, and true for perturbation theory. *Not* true for CI: energy goes as $\sqrt{n}$ for large $n$.

- Certainly, correct scaling is more desirable than an upper bound: how are we to compare systems of different sizes otherwise?
The coupled-cluster method

- Similar to CI: seeks to optimize coefficients of single and double excitations.
- Nonvariational, but exactly size-extensive.
- Much more reliable than perturbation theory or CI. CCSD (singles and doubles), CCSD(T) (adds estimate of the triples). CCSD(T) is the best Hartree-Fock based method we have.
- Approximate coupled-cluster methods: coupled-pair functional (CPF), quadratic CI (QCI).
Energy Differences for H$_2$O

H$_2$O Energy Differences ($E_h$)

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<tr>
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<th>$1.5^*r_e - r_e$</th>
<th>$2^*r_e - r_e$</th>
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<td>Full CI</td>
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**CH$_2$, DZP basis, six electrons correlated**

$^1A_1 - ^3B_1$ Separation (kcal/mol)

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## Correlated results for H$_2$O

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</table>
Correlation treatments

- $\text{H}_2\text{O}$ results with different treatments: full CI comparison (exact result in DZP basis). Coupled-cluster and MCSCF/CI methods give good results near $r_e$, latter are also excellent as bonds are stretched.

- General conclusions from full CI: multireference methods ideal but often too expensive, CC methods good bet where Hartree-Fock is reasonable. Size-extensive methods to be preferred to simple CISD. Perturbation theory not quantitatively useful.

- Basis set studies of $\text{H}_2\text{O}$: correlation effects converge much more slowly with basis set. DZP is only a starting point, need at least $f$ functions for quantitative results.
Correlation cusp

- Cusp behaviour in He

![Diagram showing Hartree-Fock and Exact correlation cusp behavior]
Basis set convergence in He

- The description of the correlation hole converges very slowly, especially in the region of the cusp:

\[
\begin{align*}
2s1p & \quad 3s2p1d \\
4s3p2d1f & \quad 5s4p3d2f1g
\end{align*}
\]
Basis set convergence in He

- Correlation energy (and wave function) converges slowly, with both radial functions and particularly angular functions.

- Contribution of a given $l$ shell to the energy can be shown to behave as $(l + \frac{1}{2})^{-4}$.

- Two-electron cusp which we’re trying to describe with a superposition of products of one-electron functions.

- Is this really a problem for larger systems, or are the basis set results good enough in practice?
Molecular properties

- Other properties, like dipole moment, polarizability, IR intensities, NMR coupling-constants, etc?

- Consider electric properties first. Molecule in a static homogeneous electric field $\vec{F}$. Classically

$$E = E_0 + \sum_i \mu_i F_i + \sum_i \sum_j \frac{1}{2} \alpha_{ij} F_i F_j \ldots,$$

where $\vec{\mu}$ is the dipole moment, and $\alpha$ is the polarizability tensor. $E_0$ is the energy out of the field, $E$ in the field.
Molecular properties

- We can also write a Maclaurin expansion

\[ E = E_0 + \sum_i \left( \frac{dE}{dF_i} \right)_{\vec{F}=0} F_i + \frac{1}{2} \sum_{ij} \left( \frac{d^2E}{dF_idF_j} \right)_{\vec{F}=0} F_i F_j \ldots . \]

Hence

\[ \mu_i = \frac{dE}{dF_i} \bigg|_{\vec{F}=0} \]

and

\[ \alpha_{ij} = \frac{d^2E}{dF_i dF_j} \bigg|_{\vec{F}=0} \]
Properties as energy derivatives

- Express properties as derivatives of the energy with respect to “applied perturbations”. E.g., harmonic force constants are second derivatives with respect to displacing the nuclei.

- Can have mixed second derivatives: differentiating once with respect to an applied electric field and once with respect to nuclear displacements gives a dipole derivative, whose square is the IR intensity.

- Differentiating with respect to an applied magnetic field gives magnetic susceptibility, etc. With respect to nuclear magnetic moments: spin-spin coupling constants, etc.

- How do we compute energy derivatives?
First derivative of the exact energy

- Exact wave function $\Psi$, assumed normalized.
  Differentiating the energy with respect to $\lambda$ gives

\[
\frac{dE}{d\lambda} = \frac{d}{d\lambda} \langle \Psi | H | \Psi \rangle
= \langle \frac{d\Psi}{d\lambda} | H | \Psi \rangle + \langle \Psi | \frac{dH}{d\lambda} | \Psi \rangle + \langle \Psi | H | \frac{d\Psi}{d\lambda} \rangle.
\]

But $H\Psi = E\Psi$, so

\[
\frac{dE}{d\lambda} = \langle \Psi | \frac{dH}{d\lambda} | \Psi \rangle + E \left\{ \langle \frac{d\Psi}{d\lambda} | \Psi \rangle + \langle \Psi | \frac{d\Psi}{d\lambda} \rangle \right\}
= \langle \Psi | \frac{dH}{d\lambda} | \Psi \rangle + E \frac{d\langle \Psi | \Psi \rangle}{d\lambda} = \langle \Psi | \frac{dH}{d\lambda} | \Psi \rangle,
\]

since the wave function is normalized to a constant (one).

- This is the *Hellmann-Feynman theorem*. 
Calculation of properties

- Since we do not know the exact wave function, we cannot simply use the Hellmann-Feynman formula.
- Must include the wave function derivatives, too.
- Can develop formulas for the energy derivatives: *analytical differentiation*; or use finite difference formulas based on explicitly including the perturbing operator in the Hamiltonian: *finite field* methods.
Calculation of properties

- Can see that if the wave function is independent of the perturbation, $d\Psi/d\lambda$ will vanish. Thus for the SCF dipole moment the Hellmann-Feynman formula is adequate (basis set is independent of an applied electric field); for forces on the nuclei we need the full derivative formula, since the basis set depends on the nuclear coordinates.

- No analogue of Hellmann-Feynman theorem for higher-order properties (i.e., higher derivatives).
### SCF properties for H₂O

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<tr>
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### SCF properties for H$_2$O

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<tr>
<th>Basis</th>
<th>$\chi \times 10^{-30}$ $JT^{-2}$</th>
<th>$\sigma$(H) (ppm)</th>
<th>$\sigma$(O) (ppm)</th>
<th>$J$(OH) (Hz)</th>
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<tr>
<td>STO-3G</td>
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<tr>
<td>STO-3G</td>
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<td>30.83</td>
<td>365.8</td>
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<tr>
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<td>32.28</td>
<td>327.8</td>
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<td>aug-cc-pVTZ</td>
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<td><strong>Experiment</strong></td>
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<td>30.052</td>
<td>344.0</td>
<td>$\pm 73.5$</td>
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</tbody>
</table>
Basis sets for properties

- Convergence is *much* worse than for structure and frequencies.
- Electric field will affect the most easily polarized part of charge density — outer fringes. Basis set must include diffuse (low-exponent) functions to describe this effect.
- Electric field multiplies wave function by $x$, $y$, or $z$, hence polarization functions (diffuse ones) are needed.
- Augment basis sets with more diffuse functions, and with polarization functions. Without these results are useless.
- Molecular properties: basis set requirements for describing perturbations complementary to those for correlation — use same strategies as when augmenting SCF sets.
Structures and vibrational frequencies

- Structures typically good to 0.002 Å or so. Vibrational frequencies to about 10 cm$^{-1}$.

- Important to include anharmonic effects to get this accuracy — molecular vibrations are not harmonic! Can be an effect of 10%.

- Must understand what experimentalists actually measure: usually lines in a spectrum (differences between quantum energy levels).

- Quantities such as bond lengths and force constants are deduced from these experimental measurements. They are not measured directly!
Case study: $P_4$

- Interest in anharmonic force fields for tetrahedral molecules ($\text{Be}_4$, $\text{CH}_4$).

- Significant disagreement between computed and experimental geometry (Häser and Treutler: best result is 0.02–0.03Å shorter than experiment).

- Experimental data for fundamental frequencies and stability with respect to $2\text{P}_2$; challenging theoretically because of contribution of correlation effects involving both core and valence. Need very accurate results to make a useful contribution.
**P₄ bond length (Å)**

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Valence</th>
<th>Valence+core</th>
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<tbody>
<tr>
<td>CCSD(T) spdf</td>
<td>2.206</td>
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<td>CCSD(T) spdfg</td>
<td>2.198</td>
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<tr>
<td>CCSD(T) spdfgh</td>
<td>2.197</td>
<td>—</td>
</tr>
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</table>

Best estimate $r_e = 2.186 \pm 0.001$

H&T estimate $r_e = 2.194 \pm 0.001$

Best estimate $r_0 = 2.191 \pm 0.001$

Expt. $r_0 = 2.2227 \pm 0.0001$ [claimed!]
**P₄ vibrational frequencies (cm⁻¹)**

<table>
<thead>
<tr>
<th>Mode</th>
<th>CCSD(T)</th>
<th>Expt.</th>
</tr>
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<tbody>
<tr>
<td>$\omega(a_1)$</td>
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<tr>
<td>$\omega(e)$</td>
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<td>$\omega(t_2)$</td>
<td>476</td>
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<td>$\nu(a_1)$</td>
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<td>600</td>
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<td>$\nu(e)$</td>
<td>374</td>
<td>361</td>
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<tr>
<td>$\nu(t_2)$</td>
<td>472</td>
<td>467</td>
</tr>
</tbody>
</table>
Case study: $P_4$

- So, we’ve exhausted our armoury and we disagree with experiment by 0.03 Å on the bond length and by up to 25 cm$^{-1}$ (!) in the vibrational fundamentals.

- In addition, the heat of the reaction

\[ P_4 \rightarrow 2P_2 \]

is estimated computationally to be 63.2 kcal/mol, whereas the experimental estimate is around 54 kcal/mol.

- Other careers begin to look attractive...
Case study: $P_4$

- Examine experimental work carefully — in order to obtain satisfactory vapour pressures of $P_4$ temperatures around 550K must be used!

- This produces significant $v = 1$ vibrational populations in all three modes. But also, enormous rotational excitation (Boltzmann population maximum at $J = 58$), which will substantially lengthen bonds and reduce frequencies.

- Ideally, solve rovibrational problem explicitly (too hard at present for these $J$ values). But estimates are not incompatible with our results.

- NIST thermochemist: “All phosphorus thermochemical results are suspect.”
Example: Carbon Clusters

- Considerable experimental interest in “bare” carbon clusters.
- Main stimulus has been fullerenes.
- What are structures of small clusters? Chains, rings, polycyclic rings? When do 3-dimensional structures appear?
Drift-tube experiments

- Smallest species emerge earliest.
- Distinguishes between 1-, 2-, and 3-dimensional structures. E.g., lots of 3D $C_{60}$.
- Typically, mainly 1D structures up to about $C_{10}$, and then mainly 2D structures up to $C_{30}$ at least.
$C_{20}$ drift-tube experiments

- No 3D structures seen. Only 2D structures (and perhaps a little 1D).

- Does this mean that the fullerene structure is less thermodynamically stable than the rings?

- Or is this a *kinetic* effect? That is, the energy barriers on pathways leading to the fullerene are too high to be overcome in these experiments?
## Calculated $\text{C}_{20}$ energetics

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Ball</th>
<th>Bowl</th>
<th>Ring</th>
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<tr>
<td>SCF</td>
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<td>MP2</td>
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<tr>
<td>CCSD(T)</td>
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<td>16</td>
<td>55</td>
</tr>
</tbody>
</table>
\textbf{C}_{20}

- According to our best calculations, the fullerene structure is the most stable thermodynamically.
- The reason it is not seen in experiment is thus due to kinetic effects. It’s very hard to “fold up” another structure into the ball!
- Some speculation about 3D structures of \textbf{C}_{24} and \textbf{C}_{28}: these have not been observed either.
- But using exactly the same computational approach, we have predicted the properties of a \textbf{C}_{6} ring, which was observed last year and confirmed the calculations. (First pure carbon ring to be identified spectroscopically.)