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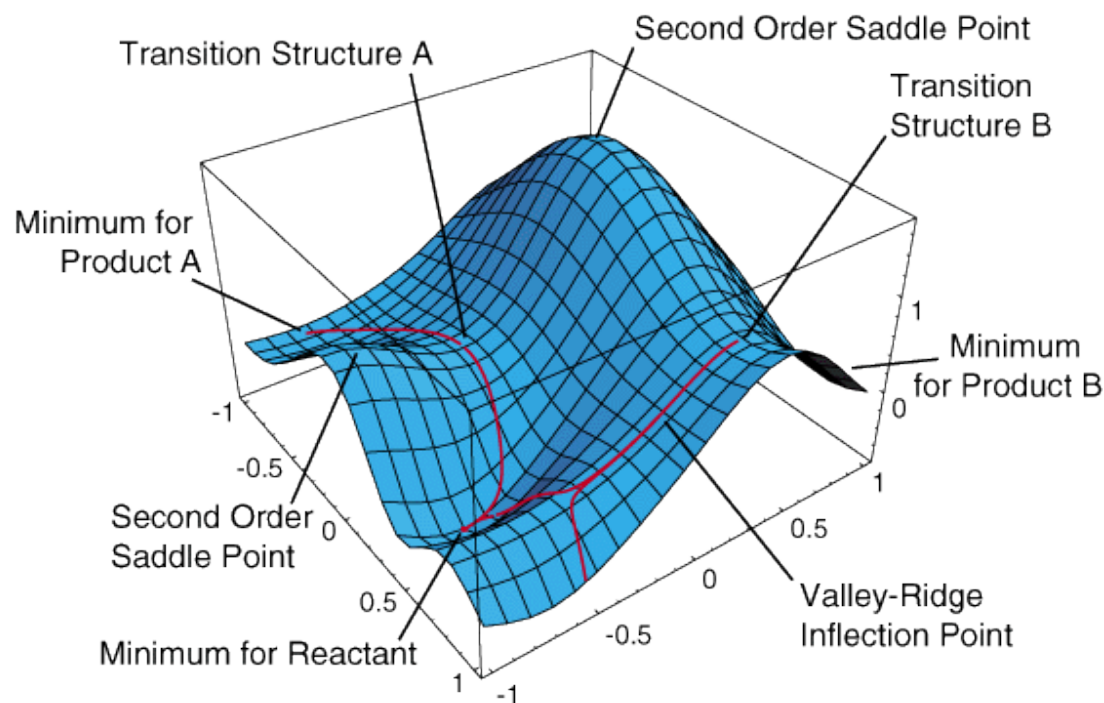
**An Introduction to the Fundamentals of  
Quantum Chemistry**

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- Describe the main concepts and arguments of *ab initio* (first principles) quantum chemistry
- Provide background context for the main methods
- Familiarity with key terminology and acronyms
- Indicate costs and benefits of popular methods

- **A single energy is not usually very useful...**
  - **Chemistry is controlled by energy differences**
- **Many important energy differences lie in the Potential Energy Surface (PES)**





- **Stable chemical structures are defined by the minima of the PES**
  - differentiating the energy w.r.t the position gives us the forces on the atoms
  - given forces, we can automatically locate minima using “geometry optimisation” techniques
- **Reaction enthalpies are from difference in well depths for reactants and products**
- **Example: a difference of approx. 1.4 kCal/mol in the barrier height corresponds to a ten-fold difference in reaction rate (standard conditions)**
- **At finite temperatures, more of the surface is accessible**
  - from forces (and nuclear masses) we can determine acceleration
  - MD is the solution of the classical equations of motion by numerical methods for a system of atoms/molecules to determine the time evolution of the system
  - Sampling can yield free energies



- **Shape of potential energy surface *close* to the minima ('harmonic approximation')** gives rise to vibrational energy levels,
  - infra-red and raman spectra
- **Some methods can also be applied to excited states**
  - usually these have similar nuclear configuration but different electronic wavefunction
  - energy difference between different states can give features of UV/vis spectra
- **Coupling of electron-electron and electron nuclear spins**
  - NMR, EPR.... spectroscopy



- In quantum chemistry we solve the *Schrödinger* equation.
- The Schrödinger equation describes the behaviour of both electrons and nuclei. It involves the kinetic energy and electrostatic interactions of all particles.
- In practice such a problem is far too hard to solve so a series of approximations is required. In brief the approximations we'll go through are
  - The time-independent Schrödinger equation
  - The Born-Oppenheimer or clamped nuclei approximation
  - The Hartree-Fock or averaged field approximation
  - The Linear Combination of Atomic Orbitals (LCAO) approximation
- This gives us a set of equations that can be solved with the Self Consistent Field (SCF) procedure using a computer.
- The approximations are not always valid and different approaches have been formulated.



- The Schrödinger eqn is given by

$$\hat{H}\Psi (r, R, t) = -i \frac{\partial \Psi (r, R, t)}{\partial t}$$

- The *Hamiltonian* operator  $\hat{H}$  involves the kinetic and electrostatic energy of all particles.

$$\hat{H} = T_{el} + T_{nuc} + V_{el-nuc} + V_{el-el} + V_{nuc-nuc}$$

$$V_{el-nuc} = - \sum_{iA} \frac{Z_A}{|r_i - R_A|}$$

$$T_{el} = - \frac{1}{2} \sum_i \nabla_i^2$$

$$V_{el-el} = \sum_{j < i} \frac{1}{|r_i - r_j|}$$

$$T_{nuc} = - \frac{1}{2} \sum_A \frac{\nabla_A^2}{M_A}$$

$$V_{nuc-nuc} = \sum_{B < A} \frac{Z_A Z_B}{|R_A - R_B|}$$

- The wavefunction squared is a probability density

$$P = \Psi^*(r, R, t) \Psi (r, R, t)$$

(note that the Hamiltonian operator does not involve time)



- As the Hamiltonian operator is time-independent and the right-hand-side of the Schrödinger equation does not involve the operators on the particle coordinates we can write

$$\Psi (r, R, t) = \Psi (r, R) \Psi (t)$$

- And substituting we get

$$\hat{H}\Psi (r, R) \Psi (t) = -i \frac{\partial \Psi (r, R) \Psi (t)}{\partial t} \quad \frac{\hat{H}\Psi (r, R)}{\Psi (r, R)} = E$$

$$\frac{\hat{H}\Psi (r, R)}{\Psi (r, R)} = - \frac{i}{\Psi (t)} \frac{\partial \Psi (t)}{\partial t} \quad 0 = - \frac{i}{\Psi (t)} \frac{\partial \Psi (t)}{\partial t}$$

- Rewriting this we get the time-independent Schrödinger equation

$$\hat{H}\Psi (r, R) = E\Psi (r, R)$$



- For the case where the Potential energy term is time-independent it is possible to
  - separate time and position dependent parts of the wavefunction
  - derive a time-independent form of the Schrödinger equation

$$\hat{H}\Psi (r, R) = E\Psi (r, R)$$

- where  $r$  and  $R$  are the position vectors for the electrons and nuclei, respectively
- One derivation can be found here  
<http://www.chemsoc.org/ExemplarChem/entries/2002/grant/schrodinger.html>



- The time-independent Schrödinger equation is still too complicated to solve.
- Further separation of variables not possible due to  $V_{el-nuc}$  but the nuclei are much slower than the electrons because of their great mass
- So assume that the nuclei are fixed (hence the name “clamped nuclei approximation”)
- This approximation equates to assuming  $T_{nuc} = 0$  and/or that the electronic motion and nuclear motion are uncoupled
- Therefore the Born-Oppenheimer Hamilton operator is

$$\hat{H} = T_{el} + V_{el-nuc} + V_{el-el} + V_{nuc-nuc}$$

- This approximation is usually valid for electronic ground states, except at “crossings” where the electronic wavefunction changes radically as a function of small movements of the nuclei (requires non-adiabatic interaction terms). In excited states these crossings are much more common than in ground states.



- We can express the Born-Oppenheimer approximation by splitting the Hamilton operator into an electronic part and a nuclear part

$$\hat{H}_{el} = T_{el} + V_{el-nuc} + V_{el-el}$$

$$\hat{H}_{nuc} = T_{nuc} + V_{nuc-nuc}$$

- And the wavefunction could be written as

$$\Psi (r, R) = \Psi (r; R)\Theta (R)$$

- Such that the Schrödinger equation becomes

$$\{\hat{H}_{el}\Psi (r; R)\}\Theta (R) + \Psi (r; R)\{\hat{H}_{nuc}\Theta (R)\} = \{E_{el}(R) + E_{nuc}\}\Psi (r; R)\Theta (R)$$

- Which in practice means that the Schrödinger equation can be solved for electrons at different nuclear configurations, after which the equation can be solved for the nuclear motion which the electronic energy as a potential



- The Schrödinger equation for the electrons still is rather complicated because of the couplings between the motion of the electrons.
- A further approximation to simplify this is the orbital approximation in which the wavefunction is expressed as a product of 1-electron wavefunctions

$$\Psi(\mathbf{r}) = \psi_1(r_1)\psi_2(r_2)\dots\psi_N(r_N)$$

- This is the so called Hartree product, which effectively leads to a “mean field” approximation where every electron feels where the every other electron is on average, instead of where every other electron is exactly.
- The Hartree product wavefunction however leads to absurd results because we have left one important thing out...



- One important aspect of quantum mechanics is the motion and position of a particle can only be known to within a certain precision simultaneously: Heisenberg's *Uncertainty Principle*.
- As a result we cannot follow the motion of particles separately and we have to assume that like particles are interchangeable.
- This leads to a permutation symmetry requirement for the many-electron wavefunction.
- From observation we find that the symmetry depends on the intrinsic magnetic moment of the particles involved:
- For half-spin particles (Fermions, i.e. electrons, quarks, He<sup>3</sup> nuclei, etc) the wavefunction must be *anti-symmetric*: *Pauli's Exclusion Principle*

$$\Psi (r_1, \dots, r_i, \dots, r_j, \dots, r_N, R) = - \Psi (r_1, \dots, r_j, \dots, r_i, \dots, r_N, R)$$

- For integer-spin particles (Bosons, i.e. photons, gravitons, He<sup>4</sup> nuclei, etc) the wavefunction must be *symmetric*.



- One way of implementing anti-symmetry is to use a *determinant*: a mathematical construct that changes sign when you swap two rows or columns.
- Considering determinants the simplest approximation we can make is representing the wavefunction by a single ('Slater') determinant

$$\Psi(\vec{r}) = \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \psi_2(\vec{r}_2) & \cdots & \psi_2(\vec{r}_N) \\ \vdots & \vdots & & \vdots \\ \psi_N(\vec{r}_1) & \psi_N(\vec{r}_2) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

- Substituting this into the electronic Schrödinger equation we have the Hartree-Fock equations (note the last term in the left-hand-side which results from the anti-symmetry)

$$\left( -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|\vec{r} - \vec{R}_A|} + \sum_j \int \frac{|\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \right) \psi_i(\vec{r}) - \sum_j \left( \int \frac{\psi_j(\vec{r}') \psi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \right) \psi_j(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$



- Finally, in order to arrive at an equation that can be solved for an arbitrary trial wave function, we multiply on both sides by the wave function (strictly, its hermitian conjugate) and integrate over all space – this gives us the so-called *pseudoeigenvalue* form of the Schrödinger Equation:

$$\int \Psi^*(r, R) \hat{H} \Psi(r, R) dr = E \int \Psi^*(r, R) \Psi(r, R) dr$$

- where  $r$  represents the coordinates of all electrons

- The Hartree-Fock equations are still rather difficult solve as the 1-electron wavefunctions  $\psi$  are rather abstract.
- To get a handle on these functions we approximate them by expressing them as linear combination of known functions called a “basis”

$$\psi_i(r) = \sum_{\mu} \chi_{\mu}(r) C_{\mu i}$$

- Different forms of functions are in use. Most commonly used are Gaussian Type Orbitals (GTO). Others are Slater Type Orbitals (STO) and Plane Waves (PW).

$$\chi_{\mu}^{\text{GTO}}(r, R) = \sum_k c_k \exp(-\alpha_k |r - R|^{\gamma}) \quad \chi_{\mu}^{\text{STO}}(r, R) = \sum_k c_k \exp(-\alpha_k |r - R|)$$

$$\chi_{\mu}^{\text{PW}}(r) = e^{-ik_{\mu} \cdot r}$$

- The GTOs and STOs are chosen to mimic Atomic Orbitals (AO) hence the name Linear Combination of Atomic Orbitals (LCAO) approximation.



- Substituting the LCAO approximation into the Hartree-Fock equation and projecting the resulting expression onto the basis we get

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad S_{\mu\nu} = (\mu | \nu)$$

$$F_{\mu\nu} = (\mu | h | \nu) + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu | \sigma\lambda) - \frac{1}{2}(\mu\lambda | \sigma\nu)] \quad P_{\mu\nu} = \sum_i C_{\mu i} C_{\nu i}$$

- Where the various things with brackets are short hand notations for integrals. Note that there are  $N^4$  2-electron integrals for  $N$  AOs.

$$(\mu | h | \nu) = \int \chi_{\mu}(r) \left( -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r - R_A|} \right) \chi_{\nu}(r) \, dr$$

$$(\mu\nu | \sigma\lambda) = \int \frac{\chi_{\mu}(r_1) \chi_{\nu}(r_1) \chi_{\sigma}(r_2) \chi_{\lambda}(r_2)}{|r_1 - r_2|} \, dr_1 dr_2$$

$$(\mu | \nu) = \int \chi_{\mu}(r) \chi_{\nu}(r) \, dr$$



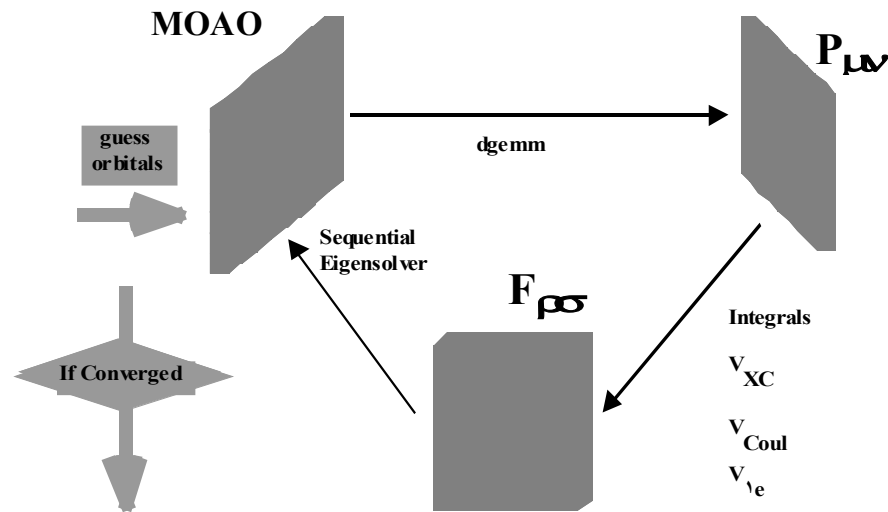
- For a particular calculation we need to choose a collection of basis functions which is called the “basis set” of a calculation.
- Pick these functions from some pre-optimised published collections also called basis sets, see <http://www.emsl.pnl.gov/forms/basisform.html>
- Looking at the general GTO expression there is some nomenclature to be aware of

$$\chi_{\mu}^{\text{GTO}}(r, R) = (x - X)^k (y - Y)^l (z - Z)^m \sum_i c_i \exp(-\alpha_i |r - R|^r)$$

- Each function is a sum (contraction) of Gaussians
  - The coefficients  $c$  are called the contraction coefficients
  - The factors  $\alpha$  are called the exponents
  - Each term is called a primitive function
- The angular momentum of the functions is fixed by the sum  $k+l+m$ 
  - A set of functions with common exponents is called a “shell”.
  - An SP or L shell has common exponents for S and P functions
  - Segmented contraction: no shared exponents
  - General contraction: all exponents shared among all functions of a given angular momentum

Ang Mom	k+l+m	#Cart	#Harm
S	0	1	1
P	1	3	3
D	2	6	5
F	3	10	7
G	4	15	9

- The LCAO equations for the coefficients  $C$  depend on these very same coefficients through  $F$ . Therefore we need an iterative process.



- Initial guess of the wavefunction
- Iteratively improve the coefficients until the coefficients going in generate the same coefficients coming out ('self consistency')



- **Closed Shell calculations**

- **RHF**

- *Same orbitals for alpha and beta spin electrons*
    - *Every occupied orbital has both an alpha and beta electron in it*

- **Open Shell calculations**

- **UHF**

- *Different orbitals for alpha and beta spin electrons*
    - *Solve alpha and beta eigenvalue equations*

- **ROHF**

- *Same orbitals for different spin,*
    - *but different occupations (more alpha electrons than beta)*

- **GVB (Generalised Valence Bond)**

- *Doubly occupied & singly occupied orbitals, bonding/anti-bonding pairs*



- **Conventional SCF**
  - Store 2-electron integrals on file
  - Efficiency improved by neglecting small integrals
- **Direct SCF**
  - Compute integrals whenever needed
  - Efficiency improved by pre-screening (taking  $C_{\sigma j} C_{\tau j}$  into account)
- **Direct vs. Conventional**
  - **Conventional:**
    - *requires less computation*
  - **Direct:**
    - *requires much less disk space*
    - *avoids I/O bottleneck - particularly important on parallel machines*



- **The main failure is the lack of electron correlation. Each electron only feels an potential of the other electrons that is averaged over all space.**
- **In reality the behaviour of any electron depends explicitly on the positions of all other electrons.**
- **There are two main ways of including correlation**
  - **Density Functional Theory**
    - *Formalism based on Hartree-Fock*
    - *Subject to the single determinant approximation*
    - *Effect of functionals is not systematic (choice is empirical)*
  - **Configuration Interaction**
    - *Rigorously lifting the single determinant approximation*
    - *Can get very expensive*



- **If you know the electron density you know everything**
  - The nuclear positions
  - The nuclear charges
  - The number of electrons
- **Functional incorporates**
  - Exchange
  - Correlation
- **Functionals**
  - Local Density
  - Gradient Corrected (GGA)
  - Hybrid
- **Numerical integration required**

- Hartree-Fock

$$K\psi_i(\vec{r}_1) = \sum_j \int \frac{\psi_i(\vec{r}_2)\psi_j^*(\vec{r}_2)}{r_{12}} dr_2 \psi_j(\vec{r}_1)$$

- Density Functional Theory

$$K\psi_i(\vec{r}_1) = f[\rho(\vec{r}_1)]\psi_i(\vec{r}_1)$$

- Hohenberg-Kohn-Sham formalism
- Assumes a charge density, and successively better approximates the Hamiltonian  
(cf. Traditional *ab initio* MO methods assume an exact Hamiltonian and successively better approximate the wave-function)



- Widely used approach that relies on the Hohenberg-Kohn theorem which states that if you know the electron density then you know everything including the exact energy.
- E. Bright Wilson: If you know the density then the cusps tell you where the atoms are, the gradient at the cusps tells you the nuclear charge, the integral over the density gives you the number of electrons, thus you know the Hamilton operator and therefore *in principle* you know the wavefunction and the energy.
- In practice DFT boils down to a modified Hartree-Fock equation

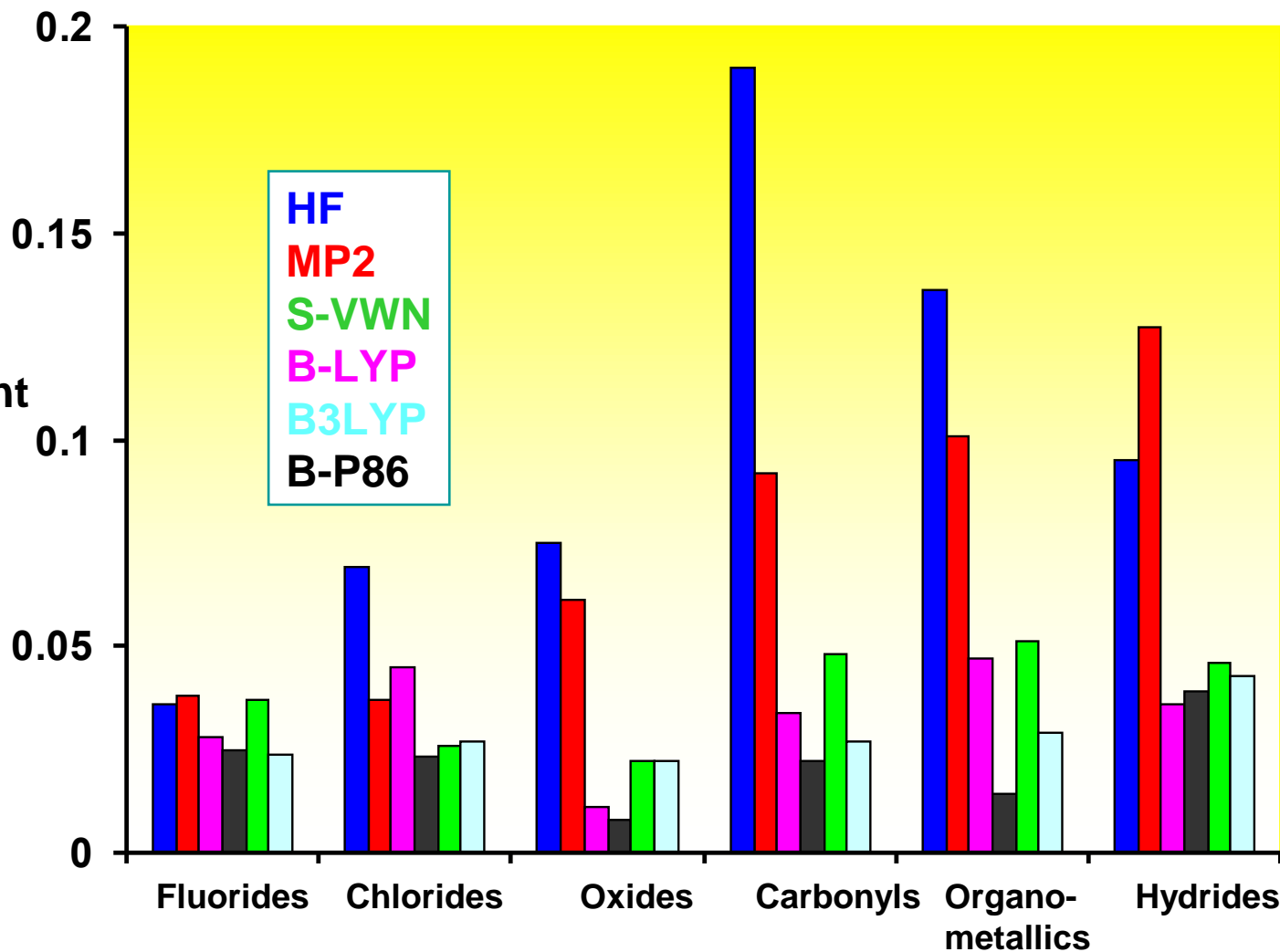
$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \sum_A \frac{Z_A}{|r - R_A|} + \sum_j \int \frac{|\psi_j(r')|^2}{|r - r'|} dr' \right) \psi_i(r) - V_{xc} \left( \sum_j |\psi_j(r)|^2 \right) \psi_i(r) = \epsilon_i \psi_i(r)$$

- Where  $V_{xc}$  is supposed to account for all exchange and correlation effects.
- The advantage is that you formally include correlation while the cost of solving these equations is very similar to Hartree-Fock
- The disadvantage is that the true  $V_{xc}$  is unknown and its approximate forms have various drawbacks.



# First-Row Transition Metal-Ligand Bond Lengths (M-L) RMS Deviations from Experiment

RMS Deviation  
(B2 basis, Å)  
from experiment



- **First derivative provides atomic forces**
  - geometry optimisation and transition state searches to locate stationary points on potential energy surfaces (PEs)
- **Second derivatives**
  - vibrational frequencies and infrared intensities
  - analytic form implemented for HF, MP2 and DFT
  - characterisation of stationary points
    - *(minima, transition states etc.)*
- **Other derivatives**
  - polarisabilities
  - magnetisability
  - Raman intensities

*Amos, R. D., 1987, in Adv. Chem. Phys., pp 99*



## From the converged wavefunction we can compute:

- **A variety of one-electron properties**
  - dipole moment
  - electrostatic potentials
  - electric field
  - electric field gradient
  - quadrupole moment
  - octupole moment
  - hexadecapole moments
  - spin densities

- Population analysis (**atomic charges, bond and orbital analysis**)
- **Generate** localised molecular orbitals (**LMOs**)
- graphical analysis (**electron density, orbital amplitude, electrostatic potential maps**)
- distributed multipole analysis (**DMA**)
- **Morokuma** energy decomposition analysis



- **Configuration Interaction, CI (dynamic correlation)**
  - Many determinants
  - Orbitals kept fixed
  - Configuration coefficients optimised
  - Perturbation expansions (e.g. MP2)
- **MCSCF, CASSCF (static and dynamic correlation)**
  - Multiple determinants
  - Simultaneous optimisation of both orbitals and configuration coefficients
  - proper dissociation of bonds, near degeneracies
  - Requires a choice of active space (partially occupied molecular orbital subset) based on
    - *Bond dissociation*
    - *Near degeneracies*
    - *Occupation numbers from a small CI calculation*



- Instead of approximating the wavefunction by a single Slater determinant we can write the wavefunction as a sum of Slater determinants

$$\Psi = \sum_I c_I |\psi_{I_1}(r_1)\psi_{I_2}(r_2)\dots\psi_{I_N}(r_N)| \quad \lambda = \sum_I c_I^\lambda$$

- Substituting this into the electronic Schrödinger equation we get

$$\mathbf{H}\mathbf{c} = \mathbf{E}\mathbf{c}$$

- However the cost of solving for the full set of coefficients is horrendous except for the smallest of molecules.
- Therefore numerous approximations based on various numbers of orbital substitutions have been developed.

$$\Psi = \Psi_{HF} + \Psi_S + \Psi_D + \dots$$



- **Møller-Plesset (MP) perturbation theory**
  - Relatively cheap
  - Often does not converge and is particularly notorious if the single determinant approximation is not valid
  - Computational effort  $N^5$  (MP2)  $N^6$  (MP4)
- **Configuration Interaction Singles-Doubles (CISD)**
  - Computational effort  $N^6$
  - Can be used to compute excited states
  - Estimate of the correlation energy worsens with system size (not size consistent)
- **Coupled Cluster (CC)**
  - Wavefunction coefficients from an exponential expansion
  - Most popular CCSD(T) singles-double plus perturbative triples
  - Computational effort  $N^7$
  - Often breaks down if the single determinant approximation fails



- **MRDCI**
  - Computes and stores all (Table-CI) or part (semi-direct) of the Hamiltonian matrix
  - Perturbatively selects the most important determinants
  - Useful for calculating excited states and UV/Vis spectra
  - semi-direct implementation extended size of systems amenable to study -  $5 \times 10^5$  configurations, 20 roots
  - *“automatic” calculation of UV/Vis spectra*
- **Direct-CI**
  - Recomputes most of the Hamiltonian matrix whenever needed
  - Uses all single and double excitations from a multireference set
  - Useful for calculating accurate ground states
  - Limited range of Excited states also possible
  - $10^7$ - $10^8$  configuration state functions
- **Full-CI**
  - Useful for benchmark energies

- For near degeneracies it is critical to re-optimize the orbitals in the context of a multi-configurational wavefunction.
- The procedure is analogous to the normal SCF procedure but with the additional step of optimising a CI wavefunction.
- The distribution of the electrons over orbitals is
  - Lowest energy orbitals doubly occupied
  - Highest energy orbitals unoccupied
  - In between are the “active” orbitals which have varying occupations depending on the CI wavefunction
  - If all possible configurations are included we have a “Complete Active Space” (CASSCF).
- Usually scales like  $N^5$
- Does not account for dynamic correlation



## 1. Configuration Interaction (CI)

- **Configuration expansion**
  - Hartree-Fock: single determinant with electrons in the lowest energy orbitals
  - Many other determinants possible
  - Multiple determinant zero-order wavefunctions
    - *a small number of determinants*
    - *near degeneracies*
    - *non-dynamic correlation*
    - *GVB, MCSCF, CASSCF*
  - Many determinant wavefunctions
    - *a large numbers of determinants (100M+)*
    - *dynamic correlation*
    - *MP, CI, CC, Full-CI*



## 2. Perturbation Theory (PT)

- **Møller-Plesset 2nd order perturbation theory (MP2) is the most efficient post-HF method**
- **Size extensive**
- **Non-variational**
- **Problems if orbital energies ( $\epsilon_i, \epsilon_a$ ) close together**
- **Functionality available**
  - **Energy (MP2, MP3)**
  - **Gradients (MP2, MP3)**
  - **Analytic frequencies (MP2)**
  - **Numerical frequencies (MP2, MP3)**
- **Both direct and conventional MP2 scheme available**



## 3. Coupled Cluster (CC)

- **Exponential expansion of the wavefunction**
- **Size extensive (size extensivity exists where the energy is a linear function of the number of particles)**
- **Non-variational**
- **CCSD ( $n^6$ ) and CCSD(T) ( $n^7$  scaling)**
- **At present only closed shell energies available in GAMESS-UK**
- **Most useful for accurate ground state energies**
- **Now widely used to obtain accurate energetics from DFT geometries**



- **Class of approaches in which properties are calculated by considering how a molecule responds to an external perturbation.**
  - Time independent reference wavefunction
  - Response to a time dependent electric field treated with a perturbation expansion
- **Eigenvalues of resulting equations correspond to excitation energies**
- **Most useful as an efficient formalism to calculate UV/Vis spectra, ionisation and attachment potentials**
- **Accuracy good for single electron excitations**
- **Tamm-Dancoff Approximation (TDA)**
  - Equivalent to a Singles CI
- **Random Phase Approximation (RPA)**
  - Includes some correlation effects with the reference state
  - Excited state gradient and geometry optimisation
- **Multi Configurational Linear Response (MCLR)**
  - RPA using a MCSCF reference wavefunction



- **Place a QM molecule in an environment consisting of other classical molecules and a dielectric media.**
  - VanDuijnen, P. T. and DeVries, A. H., 1996, *Int. J. Quantum Chem.*, 60, 1111-1132.
  - Devries, A. H., Vanduijnen, P. T., Juffer, A. H., Rullmann, J. A. C., Dijkman, J. P., Merenga, H. and Thole, B. T., 1995, *J. Comput. Chem.*, 16, 1445-1446.
  - Devries, A. H., Vanduijnen, P. T., Juffer, A. H., Rullmann, J. A. C., Dijkman, J. P., Merenga, H. and Thole, B. T., 1995, *J. Comput. Chem.*, 16, 37-55.
- **The classical surroundings may be modelled in a number of ways:**
  - by point charges to model the electrostatic field due to the surroundings
  - by polarizabilities to model the (electronic) response of the surroundings
  - by an enveloping dielectric to model bulk response (both static and electronic) of the surroundings, and
  - by an enveloping ionic solution, characterized by its Debye screening length.



- **A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. McGraw-Hill, New York, 1989.**
  - A good standard introduction to the field
- ***Modern Electronic Structure Theory*, David R. Yarkony, Ed. World Scientific Publishing, Singapore (1995).**
  - Excellent reviews of methodology
- **For a statistical survey of the accuracy of popular *ab initio* methods covering bond lengths and vibrational spectra, see <http://www.cse.clrc.ac.uk/ccg/qcr/qcr.shtml>**