CHEM30242

Electronic Structure Calculations

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Overall Content

0. Preliminaries

Sources

- *"Essentials of Computational Chemistry"*, **2nd Ed. ,
  CJ Cramer, Wiley, 2004.**

- *"Molecular Modelling. Principles and Applications"*, **2nd Ed.
  AR Leach, Addison-Wesley, 2001.**

- **"***Introduction to Computational Chemistry***" , 2nd Ed.
  F Jensen, Wiley, 2007.**

- *(Exploring Chemistry with Electronic Structure Methods"*,
  **2nd Ed., JB Foresman and Æ Frisch, Gaussian Inc,
  Pittsburgh, PA, USA, 1996).**

Big picture

What is Computational Chemistry?

"It is a chemistry branch using results of theoretical chemistry, incorporated into efficient computer programs to calculate the structures and properties of molecules and solids, applying these programs to real chemical problems."

Examples of such properties are structure, atomic charge, (interaction) energy, dipole moment, vibrational frequency, reactivity, electrostatic potential, electron density, etc.

The term "computational chemistry" is also sometimes used to cover any of the areas of science that overlap between computer science and chemistry.

**Organometallic / Catalysis / Combustion / Solar Energy
Radicals / Drug Design / Charge Transfer in DNA /Atmospheric**

1. Quantum Mechanics and the Wave Function

- **Different rules for micro- and macroscopic world.**

- **Planck, blackbody radiation is quantised.**

- **Beyond Newtonian mechanics: new mechanics.**

- **Wave mechanics -> quantum mechanics (QM).**

- **Fundamental postulate of QM:**

$$\hat{A}\Psi = e\Psi$$

- **where A = operator.**
  Ψ = wavefunction.
  e = eigenvalue.

- $$\left| \Psi^{*}\Psi \right| = \left| \Psi \right|^{2}$$ **has units of probability density.**

- **Integrate over a region of space to find probability.**

2. Hamiltonian Operator

$$\hat{H}\psi = E\psi$$

- where is H = Hamiltonian (operator)

  Ψ = wavefunction.

  E = energy.

- There are many acceptable eigenfunctions, each with its own E.

- The Schrödinger eq. is a differential equation expressing an eigenvalue problem, i.e.

Operator working on function=(scalar) x (original function).

eigenvalue   eigenvector

- Can be solved exactly for "toy" problems, e.g. particle-in-a-box, harmonic oscillator, hydrogen-like species (H, He$^+$, Li^{2+}).

- Key problem: how to solve the Schrödinger equation for an atom, molecule, molecular complex or crystalline matter?

- **Five contributions to the total energy:**

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

- **Laplacian:** $\quad \nabla_i^2 = \dfrac{\partial^2}{\partial x_i^2} + \dfrac{\partial^2}{\partial y_i^2} + \dfrac{\partial^2}{\partial z_i^2}$

- **Kinetic Energy operator:** $\quad \hat{T} = -\dfrac{\hbar^2}{2m} \nabla^2$

- **Orthonormal = 'orthogonal' and 'normal'.**

$$\iiint \Psi_i \Psi_j \, dx \, dy \, dz = \delta_{ij}$$

- **Kronecker delta (=1 if i=j; =0 otherwise)**

- **Shorthand for multiple integral (over 3n-D volume element dr).**

$$\int \Psi_i \Psi_j \, d\mathbf{r} = \delta_{ij}$$

$$\int \psi_j \hat{H} \psi_i \, d\mathbf{r} = \int \psi_j E_i \psi_i \, d\mathbf{r} = E_i \int \psi_j \psi_i \, d\mathbf{r} = E_i \delta_{ij}$$

3. The Variational Principle.

$$\Phi = \sum_{i=1} c_i \Psi_i$$

- where Φ = arbitrary (trial) function.
  - c_i = coefficients (real numbers).
  - Ψ_i = set of orthonormal wavefunctions.

- Since $\{\Psi_i\}$ is **complete**, Φ **must** be a linear combination of $\{\Psi_i\}$.

- Coefficients constrained by normality of Φ
  - derivation A (p.108)

$$\sum_{i=1} c_i^2 = 1$$

- What is the energy for this trial function?
  - derivation B (p.109)

$$E = \sum_{i=1} c_i^2 E_i$$

- Energy is bounded from below: **ground state** energy E_0.

- derivation C (p.109)

$$\frac{\int \Phi \hat{H} \Phi d\mathbf{r}}{\int \Phi^2 d\mathbf{r}} \geq E_0 \qquad \text{Eq. (VP)}$$

- The lower the energy, the better.

4. The Born-Oppenheimer Approximation

- **Full Hamiltonian for the molecular system:**

$$\hat{H} = \hat{T}_{el}(r) + \hat{T}_N(\mathbf{R}) + \hat{V}_{N-el}(\mathbf{R}, r) + \hat{V}_{el}(r) + \hat{V}_N(\mathbf{R})$$

- **Nuclei are moving very much slower than electrons.**

- **Electronic "relaxation" wrt nuclear motion is instantaneous.**

- **Hence, decouple the two motions: compute electronic energies for fixed nuclear positions.**

- **Separate the nuclear motions (R) and electronic motions (r).**

- **The B.O. approximation enables the separation of the above eq. into an electronic Schrödinger eq. (and a nuclear one).**

$$(\hat{H}_{el} + \hat{V}_N)\Psi_{el}(\mathbf{r};\mathbf{R}) = E_{el}(\mathbf{R})\Psi_{el}(\mathbf{r};\mathbf{R})$$

- **E_{el} is the 'electronic energy' or the sum of 'pure electronic energy' and V^{nuc}.**

5. Construction of a trial wavefunction.

- **Electron-nuclear correlation was removed from Schr.Eq.**

- **Remaining correlation between electrons is difficult.**

- **For now, ignore electron correlation: systems with 1 el.**

- **Call eigenfunctions of Schr.Eq. Molecular Orbitals (MOs).**

- ψ_{el} = **1-el wavefunction;** Ψ_{el} **is many-electron wfn.**

- **Energy of a MO is energy of the electron in that orbital.**

- **This MO energy = measured ionisation potential.**

- **To measure E_{el} , which includes V_N , measure atomisation energy = energy to ionise the electron and remove all nuclei to infinite separation.**

- **In practice, atomisation energy is not measured.**

6. The LCAO basis set approach.

- **Construct wavefunction (wfn) in any reasonable way.**

- **Wfn with lowest energy will be the most accurate.**

- **Expand wfn with convenient functions, called a basis set.**

  - **"The more diverse the building blocks the higher the flexibility…"**

  - **But a large basis set is more costly in terms of computer time.**

- **Temporarily working with 1 el. → solve S.Eq. exactly and obtain hydrogenic atomic orbitals 1s,2s,2p,3s,…**

- **Construct a guess wavefunction as a Linear Combination of Atomic Orbitals:**

$$\phi = \sum_{i=1}^{N} a_i \varphi_i$$

- **LCAO expansion does not specify location of basis fncs.**

- **A basis fnc can be centred on a nucleus but not required !**

- **Basis set "allows electrons to go" where their presence at higher density lowers the energy.**

- **Example of C-H σ bonding orbital:**
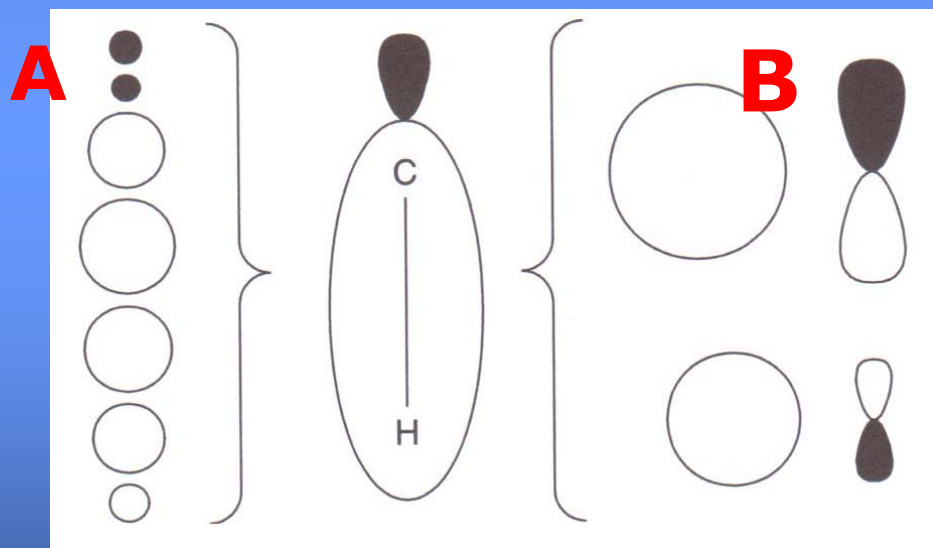
- **Caution towards chemical interpretation of coeffs. a_i .**

- **Upper limit of "N" coeffs./ Larger N spans MO space better.**

7. The secular equation.

$$E = \frac{\sum_i \sum_j a_i a_j H_{ij}}{\sum_i \sum_j a_i a_j S_{ij}}$$

- **Derivation D (p.113), from Eq.(VP) to :**

- **Matrix elements: H_{ij} resonance integral**
  S_{ij} overlap integral

- **H_{ii} : energy of single elec. occupying basis function i.**

- **Minimise the energy function as fnc of a_i. From calculus:**

$$\frac{\partial E}{\partial a_k} = 0 \quad for \ all \ k, \quad k = 1, 2, 3, ..., N$$

- **After tedious partial differentiation of eq.(4.18):**

$$\sum_{i=1}^{N} a_i (H_{ki} - E S_{ki}) = 0 \quad for \ all \ k \qquad \textbf{Eq(*)}$$

- **Set of N equations in N unknowns.**

- **Has non-trivial solution iff determinant is zero.**

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

- **This is the secular equation.**

- **Has N roots E : $\{E_1 , E_2 , ..., E_j ,..., E_N\}$.**

- **If two E_j's are equal then roots are degenerate.**

- **Each E_j leads to set $\{a_{ij}\}$, found by solving Eq(*).** $\sum_{i=1}^{N} a_i (H_{ki} - ES_{ki}) = 0$

$$\phi_j = \sum_{i=1}^{N} a_{ij} \varphi_i \quad \textbf{Eq(**)}$$

- **Summary:**

  - **Select a set of N basis functions.**

  - **For this set, determine all N^2 matrix entries H_{ij} and S_{ij}.**

  - **From the secular eq., determine all N roots, i.e. energies $\{E_j\}$.**

  - **For each of the N E_j, solve Eq.(*) and determine all a_{ij} 's for that MO.**
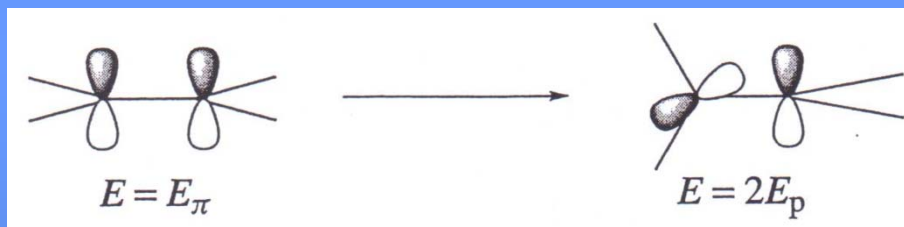
8. Hückel Theory

• **Explain unsaturated aromatic hydrocarbons (1930s).**

[1] Basis set = parallel carbon 2p orbitals, one per atom.

[2] Overlap matrix is defined by: $S_{ij} = \delta_{ij}$

[3] H_{ii} = - ionisation potential of methyl radical = α (< 0).

[4] H_{ij} between nearest neighbours also derived from exp.

$E = E_\pi \qquad E = 2E_p$

90⁰ rotation about π in ethene removes bonding interaction.

$$\Delta E = 2E_p - E_\pi$$
$$= 2\alpha - (2\alpha + 2\beta)$$
$$= -2\beta$$

Stabilisation energy of π-bond is β (<0).

[5] H_{ij} between two C(2p) orbitals more distant than nearest neighbours = 0.

9. Application to the allyl (C_3H_5) system.

- **Select 3 carbon 2p orbitals, one centred on each atom.**
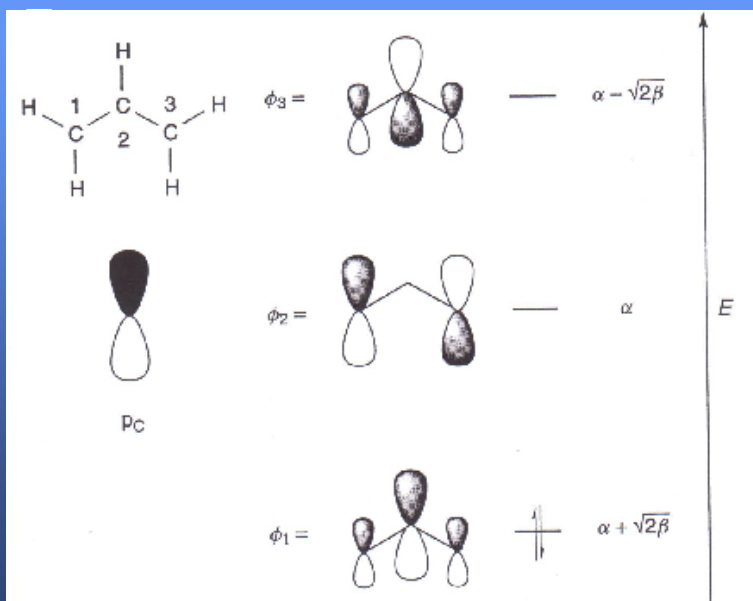
- **Set up 3x3 secular equation (N=3):**

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

- **This cubic eq. has 3 solutions, ranked from low to high E:**

$$E = \alpha + \sqrt{2}\beta, \quad \alpha, \quad \alpha - \sqrt{2}\beta$$

- **For each energy, solve the 3 eqs. in eq.(*) and obtain 3 "a" coeffs. from eq.(**). Then construct MO Φ for each**

- **antibonding**

$$\phi_3 = \frac{1}{2}p_1 - \frac{\sqrt{2}}{2}p_2 + \frac{1}{2}p_3$$

- **non-bonding**

$$\phi_2 = \frac{\sqrt{2}}{2}p_1 - \frac{\sqrt{2}}{2}p_3$$

- **bonding**

$$\phi_1 = \frac{1}{2}p_1 + \frac{\sqrt{2}}{2}p_2 + \frac{1}{2}p_3$$

10. Hartree-product

- **Assumptions so far:**
  (1) energy of a many-elec. system is the sum of energies of the occupied 1-el orbitals.
  (2) orbitals are invariant to number of elecs in the system.

- **Hückel theory incorporates elec-elec repulsion only in an average way, through α and β.**

- **Hamiltonian is separable:** $\hat{H} = \sum_{i=1}^{N} \hat{h}_i$ $\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M}\frac{Z_k}{r_{ik}}$

- **1-el Schröd.Eq.:** $\hat{h}_i \psi_i = \varepsilon_i \psi_i$

- **Hartree product:** $\Psi_{HP} = \psi_1 \psi_2 ... \psi_N$

- **Derivation E (p.120) :** $\hat{H}\Psi_{HP} = \left(\sum_{i=1}^{N} \varepsilon_i\right)\Psi_{HP}$ $\int |\Psi_{HP}|^2 d\mathbf{r} = 1$

11. The Hartree Hamiltonian

- **Interelectronic repulsion** must be included.

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M}\frac{Z_k}{r_{ik}} + V_i\{\psi_j\}$$

- where 3rd term is interaction potential for elec *i* with all other electrons occupying orbitals {ψ_j}:

$$V_i\{\psi_j\} = \sum_{j\neq i}\int\frac{|\psi_j|^2}{r_{ij}}\,d\mathbf{r}$$

- But how can {ψ_j} be used before they are known?

- Iterative method: **"Self-consistent field (SCF)".**

- First step: guess the wavefunctions ψ for all occupied MOs.

- Next steps: solve $\hat{h}_i\psi_i = \varepsilon_i\psi_i$ to obtain a new set of ψ.

- Final step: {ψ_j} is converged (criterion e.g. ΔE < 10^{-6} a.u.)

- Tighter convergence --> more SCF cycles --> more computing.

- Total energy E?

$$E = \langle\Psi_{HP}|\hat{H}|\Psi_{HP}\rangle = \sum_i\varepsilon_i - \frac{1}{2}\sum_{i\neq j}\iint\frac{|\psi_i|^2|\psi_j|^2}{r_{ij}}\,d\mathbf{r}_i\,d\mathbf{r}_j$$

12. Electron Spin and antisymmetry

- **The Hartree product replaces 1 n-electron problem by n 1-electron problems but...**

- **We cannot ignore electron spin !**

- **Pauli exclusion principle: no two electrons can be characterised by the same set of quantum numbers.**

- **Hence, in a given MO, there can be no more than two elecs: α and β.**

- **Spin functions: α for spin up (+1/2). or β for spin down (-1/2).**

$$\alpha(\uparrow) = 1 \quad \alpha(\downarrow) = 0$$
$$\beta(\downarrow) = 1 \quad \beta(\uparrow) = 0$$

- **Spin orbital = Molecular Orbital (ψ) × spin function (α or β).**

$$\chi_k(i) = \psi_k(\mathbf{r}_i)\alpha(s_i) \ or \ \psi_k(\mathbf{r}_i)\beta(s_i)$$

for electron i and orbital k

- **In order to obey the Pauli principle the wavefunction must be antisymmetric, or**

$$\Psi(1,\ldots,i,\ldots,j,\ldots,n) = -\Psi(1,\ldots,j,\ldots,i,\ldots,n)$$

- **This means that an interchange of electronic coordinates leads to a sign change in the wfn.**

- **Problem: the Hartree product violates the Pauli principle.**

- **Hartree-product (for example, triplet or same-spin (e.g. α / α))**

$$^{3}\Psi_{HP} = \chi_1(1)\chi_2(2) \qquad \left(= \left[\psi_a(1)\alpha(1)\right]\left[\psi_b(2)\alpha(2)\right]\right)$$

$$\hat{P}_{12}\left[\chi_1(1)\chi_2(2)\right] = \chi_1(2)\chi_2(1) \neq -\chi_1(1)\chi_2(2)$$

- **Solution: create antisymmetrised orbital:**

$$\Psi_{antisymmetric}(1,2) = \frac{1}{\sqrt{2}}\left[\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)\right]$$

$$\Psi_{antisymmetric}(2,1) = \frac{1}{\sqrt{2}}\left[\chi_1(2)\chi_2(1) - \chi_1(1)\chi_2(2)\right] = -\Psi_{antisymmetric}(1,2)$$

13. Slater Determinant

- **For generalisation, rearrange in a 2x2 determinant:**

$$^3\Psi_{SD} = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1)\alpha(1) & \psi_b(1)\alpha(1) \\ \psi_a(2)\alpha(2) & \psi_b(2)\alpha(2) \end{vmatrix}$$

- **Swapping coordinates 1 and 2 is equivalent to interchanging the two rows, which is compatible with the determinant's sign change.**

- **Slater determinant:**
$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \dots & \chi_N(N) \end{vmatrix}$$
or compactly

$$\Psi_{SD} = \mid \chi_1 \chi_2 \chi_3 \cdots \chi_N >$$

- **Every electron appears in every spin orbital due to the indistinguishability of electrons.**

- **One can show that:**
$$\int \mid ^3\Psi_{SD} \mid^2 d\mathbf{r}_1 ds_1 d\mathbf{r}_2 ds_2 = 1$$

- **Interelectronic repulsion between same-spin orbitals:**

$$\int {}^{3}\Psi_{SD} \frac{1}{r_{12}} {}^{3}\Psi_{SD}\, d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 = \int |\psi_a(1)|^2 \frac{1}{r_{12}} |\psi_b(2)|^2\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$-\int \psi_a(1)\psi_b(1) \frac{1}{r_{12}} \psi_a(2)\psi_b(2)\, d\mathbf{r}_1 d\mathbf{r}_2 = J_{ab} - K_{ab}$$

- **Classical Coulomb repulsion energy between electron clouds in orbitals *a* and *b* (J_{ab}) is reduced by the exchange integral K_{ab}.**

  - **Reduced probability of finding two electrons of same-spin electrons close to one another is due to the Fermi hole.**

  - **Singlet wfn:** $$\Psi_{SD} = \frac{1}{\sqrt{2}}\left[\psi_a(1)\alpha(1)\psi_b(2)\beta(2) - \psi_a(2)\alpha(2)\psi_b(1)\beta(1)\right]$$

- **Interelectronic repulsion between different-spin orbitals:**

$$\int \Psi_{SD} \frac{1}{r_{12}} \Psi_{SD}\, d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 = J_{ab}$$

14. Hartree-Fock (HF) SCF method.

- **Fock proposed the extension of Hartree's method to Slater determinantal wfns. Now the interaction of each electron with the static field of all other electrons includes exchange effects.**

- **Roothaan introduced matrix algebra to enable HF calculations with basis sets.**

- **Restricted Hartree-Fock (RHF): formalism for closed-shell systems.**

- **One-electron Fock operator:**

$$\hat{f}_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{nuclei}\frac{Z_k}{r_{ik}} + \hat{V}_i^{HF}\{\psi_j\}$$

- **Follow the procedure of Hückel to find roots E_j :**

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & ... & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & ... & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & ... & F_{NN} - ES_{NN} \end{vmatrix} = 0$$

- **Elements of the Fock matrix are computed explicitly:**

$$F_{\mu v} = \left\langle \mu \left| -\frac{1}{2}\nabla^2 \right| v \right\rangle - \sum_k^{nuclei} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| v \right\rangle + \sum_{\lambda \sigma} P_{\lambda \sigma} \left[(\mu v \mid \lambda \sigma) - \frac{1}{2}(\mu \lambda \mid v \sigma) \right]$$
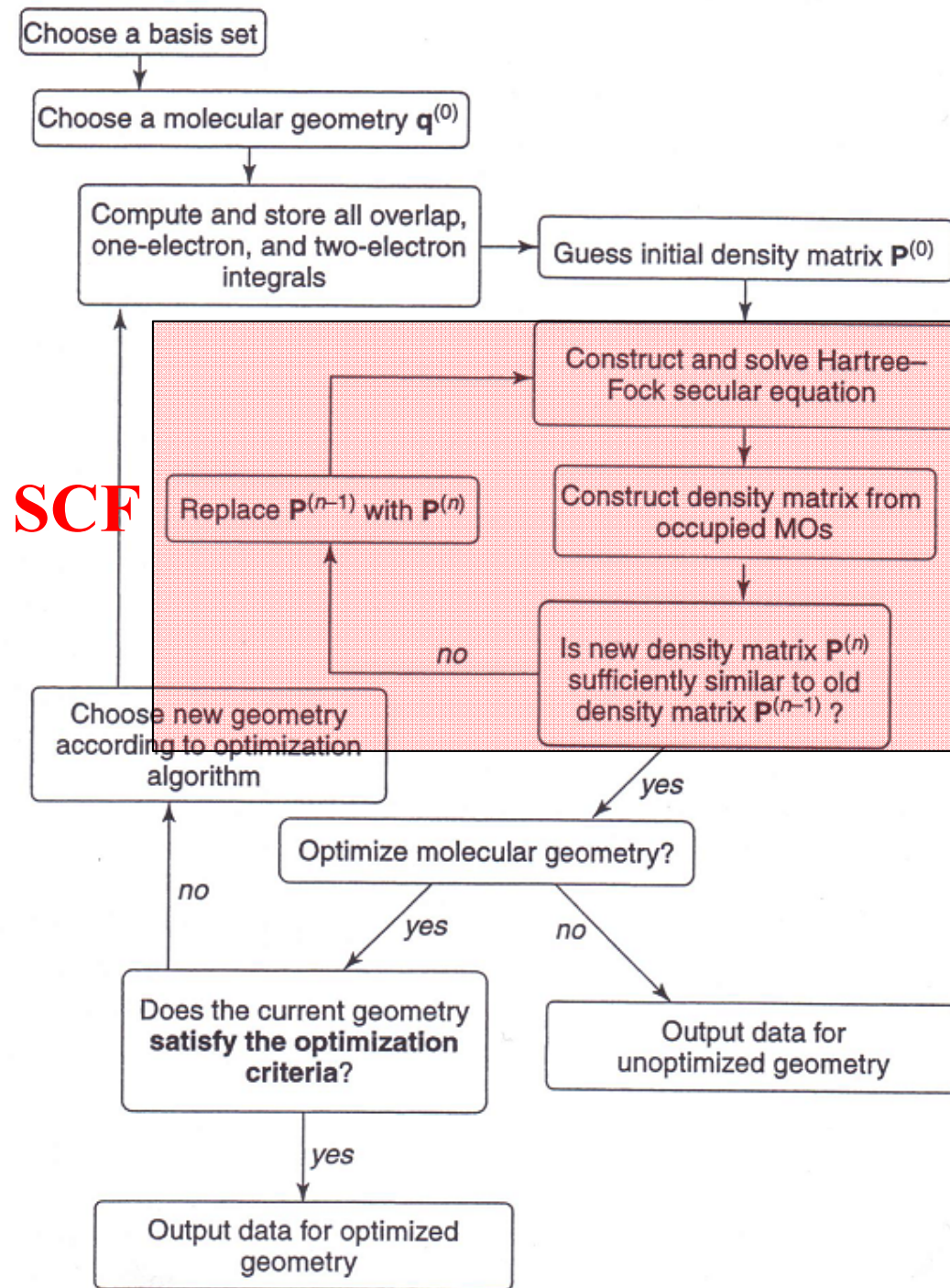
where

$$\left\langle \mu \mid \hat{g} \mid v \right\rangle = \int \varphi_\mu \, \hat{g} \, \varphi_v \, d\mathbf{r}$$

$$(\mu v \mid \lambda \sigma) = \iint \varphi_\mu(1)\varphi_v(1)\frac{1}{r_{12}}\varphi_\lambda(2)\varphi_\sigma(2) \, d\mathbf{r}(1)d\mathbf{r}(2)$$

$$P_{\lambda \sigma} = 2 \sum_i^{occupied} a_{\lambda i} \, a_{\sigma i}$$

- **Density matrix P** **describes the degree to which basis functions φ contribute to the many-electron wfn.**

- **"Paradox": to set up the Fock matrix we need to know the orbital coeffs. (i.e. *P*) but the purpose of solving the secular eq. is finding those coeffs.   Hence, again SCF procedure.**

15. Ab initio philosophy

- **Neglect of electron correlation can affect chemical properties.**

- **Two alternative philosophies:**
  - **Parameterisation → semi-empirical methods (short-term predictions, practical)**
  - **Ab initio theory → reach HF limit and use as stepping stone (long-term predictions, rigorous)**

- **HF limit = Solve Hartree-Fock equations with "infinite" basis set with no additional approximations.**

- **(Electron) correlation energy:**

$$E_{corr} = E_{exact} - E_{HF,\,limit}$$

E

HF with small basis set

HF with large basis set

HF limit

exact
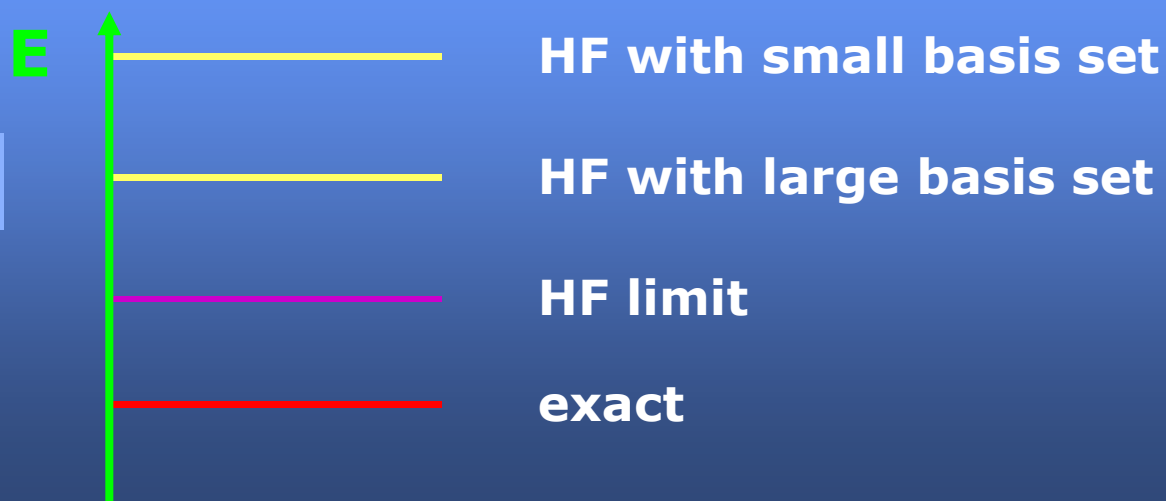
16. Basis sets (general)

- **Infinite basis set is impossible but reach this limit efficiently.**

- **Number of two-electron integrals increases as N⁴.**
  So, for sake of efficiency:

  - keep total number of basis functions *N* to a minimum.

  - functional form for computationally efficient integral evaluation.

  - useful in a chemical sense
    (large amplitude where electron density is large).

- **The natural basis functions for the molecular S.Eq. are Slaters.**

$$\varphi(r,\theta,\phi\,;\zeta,n,l,m) \;\propto\; r^{n-1}e^{-\zeta r}Y_l^m(\theta,\phi)$$

  where exponent ζ ("zeta") depends on the atomic number
  and *Y* is a spherical harmonic function (see H atom).

- **Problem: for Slaters no (easy) analytical integration of the**
  four-index (or "2-electron") integral (μν|λσ) exists.

17. Gaussian basis sets

- **Change radial decay from exp(-r) to exp(-r^2).**

- **AO-like functions are chosen to have a Gaussian form.**
  Gaussian-type orbital (GTO):

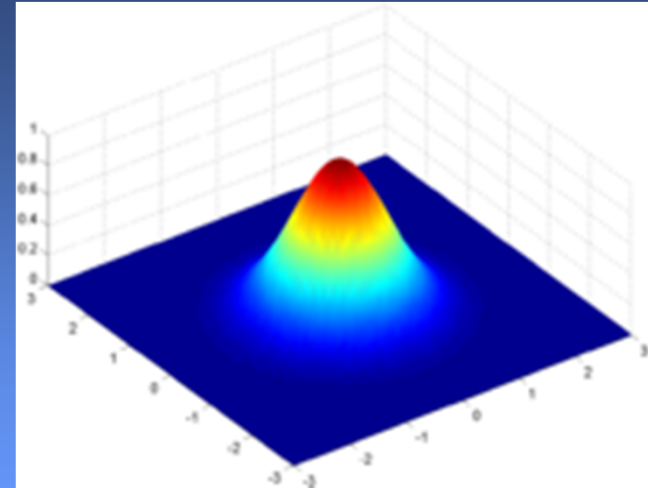$$\phi(x, y, z; \alpha, i, j, k) \propto x^i y^j z^k e^{-\alpha(x^2 + y^2 + z^2)}$$

    where exponent "alpha" controls the width of the GTO and

    i, j, k (all >0) determine s, p, d, f, ... character.

- **Examples in one dimension (1D):**

- **Three parameters determine**
  shape and position:
  - **centre (μ)**
  - **width (σ)**
  - **height (or amplitude)**
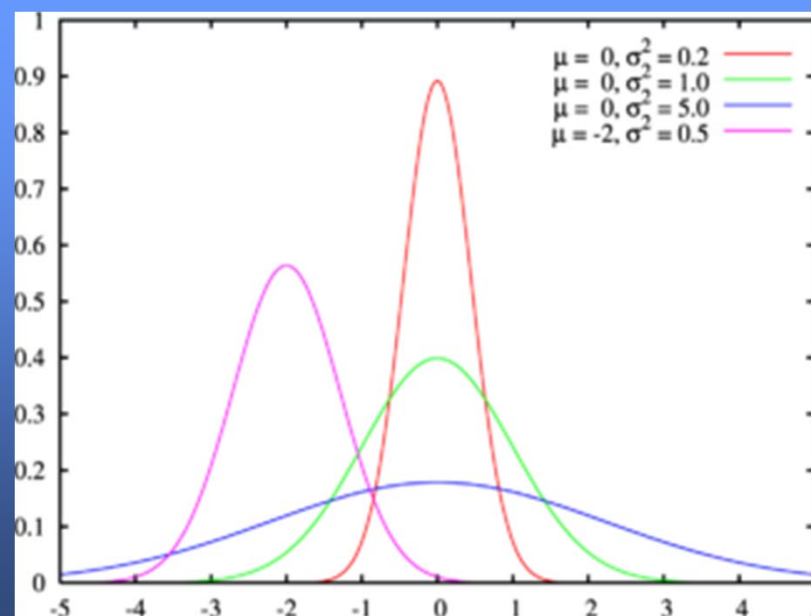
- **Example in two dimensions (2D):**

$$g(x, y) = \exp\left(-\frac{1}{2}x^2 - \frac{1}{2}y^2\right)$$

- **In three dimensions (3D):**

  - **centre: nuclear position**

  - **"width" : α**

$$g(\alpha, \mathbf{r}) = c\, x^i y^j z^k\, e^{-\alpha r^2}$$

  - **"height" : normalisation constant**

  - **prefactors in x,y and z:**
    directionality / protrusion in certain directions.

  - **Example:**
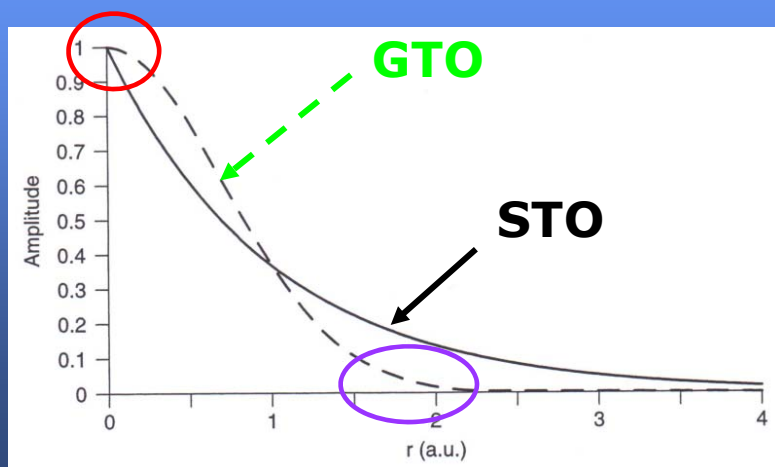
$$g_{xy}(\alpha, \mathbf{r}) = \left(\frac{2048\,\alpha^7}{\pi^3}\right)^{\!\frac{1}{4}} xy\, e^{-\alpha r^2}$$

- **If i=j=k=0 then spherical symmetry: s-type GTO.**

- **If only one index equals 1 then axial symmetry about the corresponding Cartesian axis: p-type GTO.**

- **If the sum of two indices equals 2 then d-type GTO.**

- **Six possibilities: x^2, y^2, z^2, xy, xz and yz.**

- **But only 5 d-functions span all possible values of L_z for $\ell=2$: xy, xz, yz, x^2-y^2, $3z^2 - r^2$.**

18. Contracted Gaussian functions

- **Problems with GTOs:**
  - **GTO has no cusp at r=0 but a real hydrogenic AO has.**

- **GTO decays too rapidly.**

- **Combine computational efficiency of GTO with proper radial shape of STO: linear combination of GTOs.**

$$\varphi(x, y, z; \{\alpha\}, i, j, k) = \sum_{a=1}^{M} c_a \phi(x, y, z; \alpha_a, i, j, k)$$

- **φ is a contracted basis function and Φ is a primitive Gaussian.**

- **M is the degree of contraction.**

- **Radial nodal behaviour (e.g. 2s orbital) is now possible because c_a can be negative.**

- **Example: STO-MG (M=2, 3, 4, 5 or 6)**

$$(\mu\nu \mid \lambda\sigma) = \iint \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2)\, d\mathbf{r}(1)d\mathbf{r}(2) =$$

$$= \sum_{a_\mu=1}^{M_\mu}\sum_{a_\nu=1}^{M_\nu}\sum_{a_\lambda=1}^{M_\lambda}\sum_{a_\sigma=1}^{M_\sigma} c_{a_\mu} c_{a_\nu} c_{a_\lambda} c_{a_\sigma} \iint \phi_{a_\mu}(1)\phi_{a_\nu}(1) \frac{1}{r_{12}} \phi_{a_\lambda}(2)\phi_{a_\sigma}(2)\, d\mathbf{r}(1)d\mathbf{r}(2)$$

- **Optimum speed and accuracy achieved at M=3 -> STO-3G.**

- **Example: matching the STO (ζ=1) for the H 1s function.**
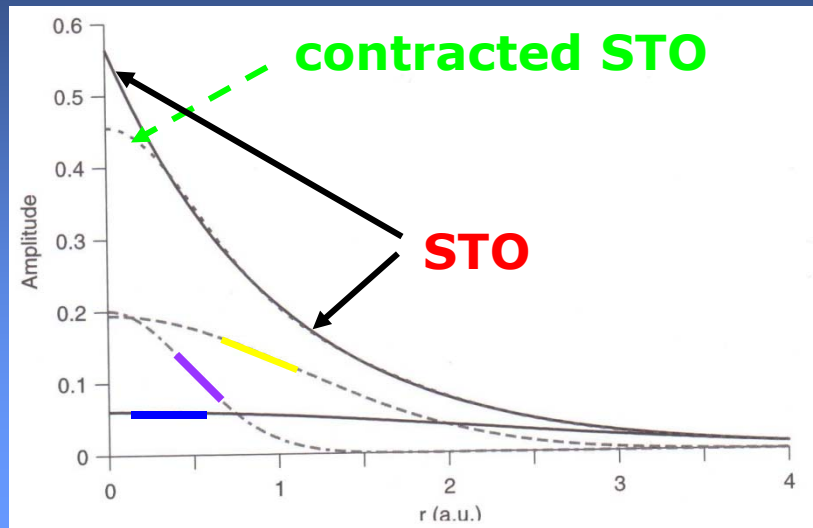
- **Contracted STO (STO-3G) is sum of tight, medium and diffuse GTO.**

- **From 0.5 to 4 a.u. STO-3G matches very well.**

19. Single-ζ, Multiple-ζ and Split-Valence

- **STO-3G is a single-ζ basis set or a minimal basis set.**

- **Only 1 basis function for each type orbital from core to valence.**
  Examples: for H -> 1s,   for C -> 1s, 2s, $2p_x$, $2p_y$ and $2p_z$,   and
  for Na -> 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$ and $3p_z$.

- **Increase the flexibility of the basis set and decontract it.**

- **Example: instead of STO-3G -> Double-ζ basis set.**
  Now two basis functions for each AO:
  (1) contract first two Gaussian primitives
  (2) normalise third primitive

- **Decontract further: triple-ζ basis set.**

- **Example: cc-pCVDZ   (of Dunning _et al._)**
  "correlation consistent polarised Core and Valence Double Zeta"

- **Advantage: approach HF limit.**

- **Core orbitals are weakly affected by chemical bonding but valence orbitals can vary widely as a function of bonding.**

- **Thus gain efficient flexibility by splitting valence orbitals into arbitrarily many functions, and represent core orbitals by a single function. Split-valence basis set.**

- **Examples: 3-21G, 6-21G, 4-31G, 6-31G and 6-311G.**

20. Polarisation Functions

- **Problem: experimental inversion barrier between two equivalent pyramidal minima in NH_3 = 24 kJmol^{-1}.
  But HF calc. predicts planar geometry to be minimum !**

- **MOs require more mathematical flexibility than do atoms.**

- **Example: Enhance O-H bonding interaction in H_2O.**
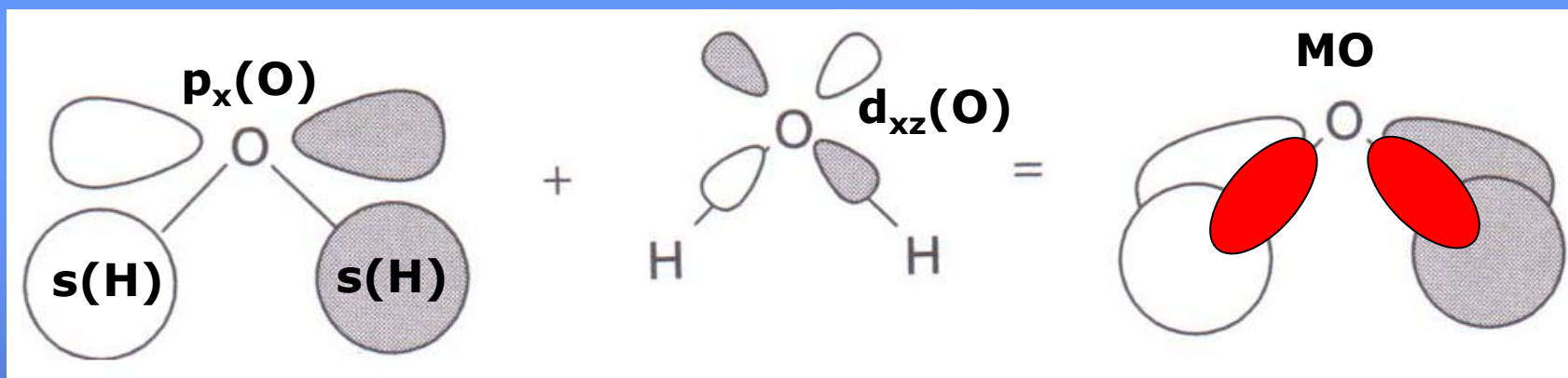
- **Add basis function of one quantum number of higher angular momentum than the valence orbitals:**

  H   : add p GTOs

  Li -->Ne : add d GTOs

- **Example: 6-31G*   means add d functions on [Li-Ne] to polarise the p functions in 6-31G (see H$_2$O example).**

- **6-31G** means add p functions on H [and He].**

- **Better nomenclature: 6-31G(d)
     because generalisation easier: e.g. 6-31G(3d2fg,2pd)**

21. Diffuse functions

- **Highest-energy MOs of anions, highly excited electronic states and supermolecular complexes are more spatially diffuse.**

- **Small exponent α. Rule of thumb: ~ 4x smaller than smallest valence exponent.**

- **Example: 6-31+G(d)   (Pople family of basis sets)
     "Heavy atoms" (Li - Ne) augmented by an s and p function.**

- **Second "plus" indicates presence of diffuse functions on H. Example: 6-311++G(3df,2pd).**

- **Example: aug-cc-pVTZ   (Dunning family). 1 diffuse function added for each angular momentum already present.**

22. HF limit

- **Extrapolate to "infinite" basis set.**

- **Dunning basis set cc-pVnZ (n=2, 3, 4, 5, 6,...) were designed for this purpose: cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z,...**
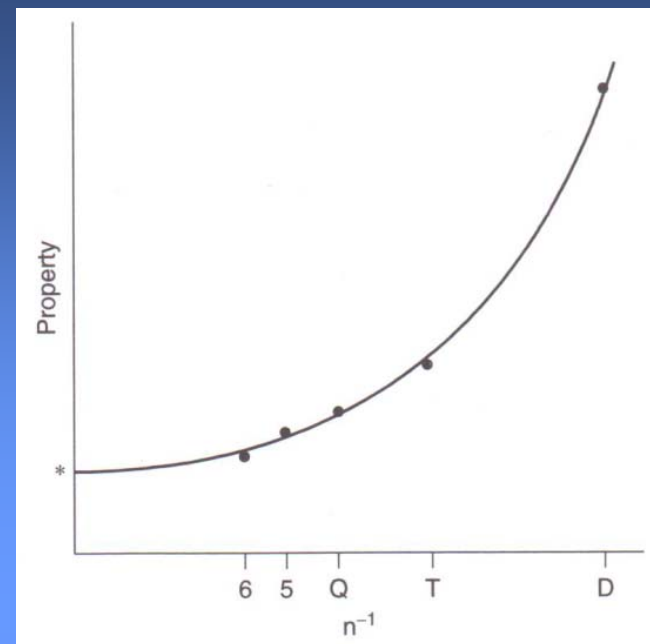
23. Miscellaneous practical points of HF.

- **SCF convergence problems:**
    - **SCF oscillation: SCF bounces between $P^{(a)}$ and $P^{(b)}$ (energy also oscillates between values).**

- **Complete basis set (or with many diffuse functions) near-linear dependencies -> MOs cannot be made orthogonal -> numerical instability.**

- Increase computational efficiency:
  - **Direct SCF:** recompute 4-index (2-elec) integrals
    rather than store them to hard disk and retrieve them.

- Estimate upper bounds for 4-index integrals.
  If integral makes no significant contribution then set it to 0.

- Optimise geometry first at lower **level of theory.**
  Then take this geometry as starting point for new
  geometry optimisation at higher level of theory.

- Use molecular symmetry (point groups).

24. Performance of HF theory

- No realistic heats of formation
  (because HF ignores electron correlation).

- Conformational energy changes.
  Example: RMS error for 35 organic molecules at
  HF/6-31+G(d,p) // HF/6-31G(d) = 2.4 kJmol^{-1}.

- **Incapable of modelling dispersion interaction (London forces). Hence intermolecular distances in complexes will be too large.**

- **For minimum-energy structures, HF geometries are very good when using at least polarised valence-double-ζ basis sets.**
  - $\Delta_{bond\text{-}length}$ = 0.03 Å between "heavy atoms".
  - $\Delta_{bond\text{-}length}$ = 0.015 Å between heavy atom and H.
  - $\Delta_{bond\text{-}angle}$ = 1.5^0
  - Dihedral angles fairly well predicted but
    - experimental data in the gas phase are scarce.

- **Predicted geometries at HF degrade in quality with increasing basis set. Why?**

- **Because HF overemphasises the occupation of bonding orbitals. Thus bonds will be too short. This effect becomes more pronounced approaching saturated basis sets.**

- **HF predicts molecules to be too polar. With valence-double-ζ basis sets the dipole moment is overestimated by 10-25%.**

25. Density Functional Theory (DFT).

- **The wave function is not intuitive for more than one electron.**

- **Explore the use of a physical observable to determine the energy of a molecule, e.g. the electron density ρ(r).**

- **Can the Hamiltonian be constructed from ρ(r)? If so, the wave function can be obtained, and thus all molecular properties!**

- **Hamiltonian depends only on (1) positions (r_k), (2) atomic numbers (Z_k) & (3) the total number of electrons, N.**

- **N can be obtained from ρ(r):** $$N = \int \rho(\mathbf{r})d\mathbf{r}$$

- **r_k can be obtained from ρ(r) because the cusps in ρ(r) coincide with the nuclear positions.**

- **Z_k can also be obtained from the electron density, spherically averaged around nucleus k.**

26. Early Functionals.

- **Roots of DFT go back to origin of quantum mechanics(1920s) but its modern form dates from 1964.**

- **DFT estimates the correlation energy in less CPU time than classic post-HF methods (e.g. 2nd order Møller-Plesset or MP2).**

- **What is a functional? A function of a function, rather than of a number (or even a set of numbers, e.g. a vector.)**

- **Example: the area under a 1D curve (in a given interval).**
  $A[f(x)] \rightarrow A[x^2]$, $A[\cos(x)]$, $A[e^x]$, ...

- **Here the energy is a functional of the electron density, $E[\rho(r)]$.**

- **Partition the total energy:**

$$V_{ne}[\rho(\mathbf{r})] = \sum_{k}^{nuclei} \int \frac{Z_k}{|\mathbf{r} - \mathbf{r}_k|} \rho(\mathbf{r}) d\mathbf{r}$$

$$V_{ee}[\rho(\mathbf{r})] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- **But what about the kinetic energy of an electron density?**

- **Introduce fictitious substance called uniform electron gas.** Infinite number of electrons in an infinite volume with a uniformly distributed positive charge.

- **Thomas and Fermi derived the kinetic energy for this system:**

$$T[\rho(\mathbf{r})] = c \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$$

- **$V_{ee}[\rho(r)]$ ignores (electron) correlation and exchange:**

$$\langle \Psi | \sum_{i<j}^{electrons} \frac{1}{r_{ij}} | \Psi \rangle = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)h(\mathbf{r}_1;\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- **hole function h corrects for this shortcoming.**

- **Fermi (exchange hole) is 10-100 larger than correlation hole. Slater ignored the latter and proposed:**

$$E_x[\rho(\mathbf{r})] = c' \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

27. Hohenberg-Kohn existence theorem.

- **The ground-state properties of a many-electron system are uniquely determined by an electron density.**

- **Omit the proof that the (non-degenerate) ground-state electron density determines the external potential (and thus the Hamiltonian).**

- **Practical problem: theorem gives no indication of how to predict the electron density of the system.**

28. Hohenberg-Kohn variational theorem.

- **Just as with MO theory, the electron density obeys a variational principle.**

- **Practical problem: how to improve candidate electron densities?**

- **We still don't know what the exact functional is, only that it exists.**

29. Kohn-Sham (KS) SCF methodology

- **Key idea: start with a fictitious system of *non-interacting (ni)* electrons that have for their overall ground-state (electron) density the _same_ density as the *real* system of interest, where the electrons *do* interact.**

- **New energy partitioning:**

$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})]$$

$$E[\rho(\mathbf{r})] = \sum_i^N \left(\langle \chi_i | -\frac{1}{2}\nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k^{nuclei} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} | \chi_i \rangle \right) + \sum_i^N \langle \chi_i | \frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|}d\mathbf{r}' | \chi_i \rangle + E_{xc}[\rho(\mathbf{r})]$$

where *N* is the number of electrons.

- We cast all into the HF SCF scheme but note presence of E_{xc}.

- Find orbitals χ_i that minimise the energy $E[\rho(r)]$.

$$\hat{h}_i^{KS} \chi_i = \varepsilon_i \chi_i$$

- where

$$\hat{h}_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \hat{V}_{xc}$$

- Note that, unlike in HF, orbitals should provide the exact electron density, since $E[\rho(r)]$ is in principle exact.

- As in HF, use basis functions Φ to set up the equivalent of the Fock matrix, now K:

$$K_{\mu\nu} = \left\langle \phi_\mu \,|\, \hat{h}_i^{KS} \,|\, \phi_\nu \right\rangle$$

- Proceed by solving the secular equation.

30. Exchange-correlation functionals.

- **DFT is exact, in principle, but the exact E_{xc} is the holy grail.**

- **Local Density Approximation (LDA): only need ρ, in one point.**
  Example: Xα model.

- **Non-local DFT: gradient corrected, now $|\nabla\rho(\mathbf{r})|$ features.**
  generalised gradient approximation (GGA)
  Examples: B86, PBE, LYP.

- **Hybrid functionals. Fit parameters against enthalpies of**
  formation for a test set of molecules.

- **most popular modern functional: B3LYP.**

31. Adiabatic Connection Methods

- **Imagine smooth conversion of the non-interacting KS**
  reference system to the real, interacting system.

$$E_{xc} = \int_0^1 \langle \Psi(\lambda) | \hat{V}_{xc}(\lambda) | \Psi(\lambda) \rangle \, d\lambda$$

where λ describes the extent of interelectronic interaction
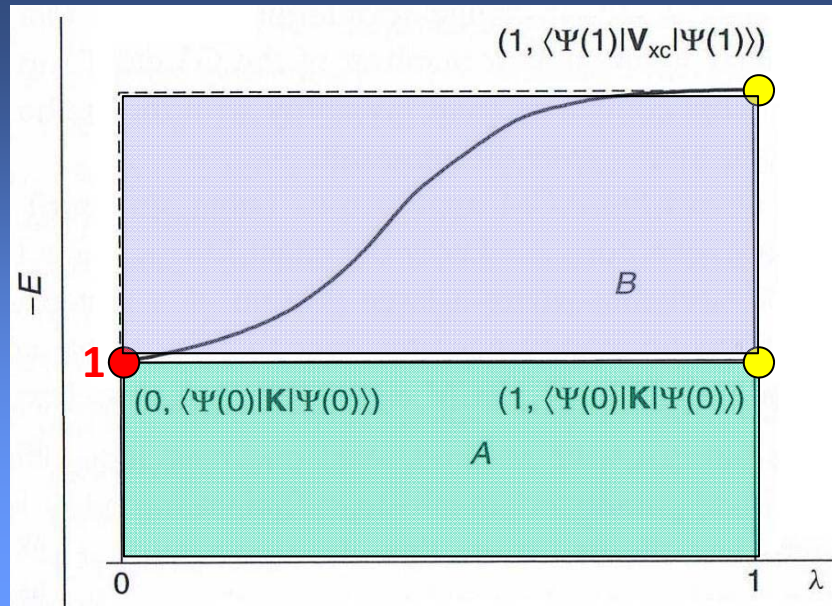
- λ=0 (no interaction)
  λ=1 (exact interaction)

- **Task: seek area under curve**
  (**A** + fraction of **B**)

- **At "1" the only component**
  of V is exchange, so V_{xc}=K

- **Area A is E_X^{HF}**

- **Remaining area B (under curve) is fraction z of** upper
  rectangle's area.

$$E_{xc} = E_x^{HF} + z(E_{xc}^{DFT} - E_x^{HF})$$

- **We do not know z but optimise it as an empirical constant.**

$$E_{xc} = (1-a)E_{xc}^{DFT} + aE_x^{HF} \quad ; \quad a = 1-z$$

$$E_{xc}^{B3LYP} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^{B} + (1-c)E_c^{LSDA} + cE_c^{LYP}$$