CHEM 545

Theory and Practice of Molecular Electronic Structure

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"Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry - an aberration which is happily almost impossible - it would occasion a rapid and widespread degeneration of that science."

A. Comte (1830)

Contents

Chapter 1

Introduction

The Royal Swedish Academy of Sciences has awarded the 1998 Nobel Prize in Chemistry in the area of quantum chemistry to Walter Kohn and John Pople. The prize was awarded for pioneering contributions in developing methods that can be used for theoretical studies of the properties of molecules and the chemical processes in which they are involved. The prize was divided equally between: "Walter Kohn for his development of the density-functional theory and John Pople for his development of computational methods in quantum chemistry".

Why where advances in this field so highly recognized? What questions are covered by electronic structure theory?

1. The equilibrium structures of molecules and their excited states;
2. Molecular properties: electrical, magnetic, optical, etc.;
3. Spectroscopy, from NMR to X-ray;
4. Intramolecular interactions, transition states, and reaction paths: reaction mechanisms in chemistry and biochemistry;
5. Intermolecular interactions giving potentials which may be used to study macromolecules, solvent effects, crystal packing, etc.

Here we are concerned with two types of answers: *quantitative* and *qualitative*. Knowledge of the spectrum/geometry for some unstable radical can help to design experiment. On the other hand, calculations can help to interpret results of the experiment, e.g., to assign complicated spectra, or to establish mechanism of a reaction.

The goal of this class it to provide a guide to electronic structure calculations. More specifically, to *ab initio* calculations of electronic structure. "Ab initio" means "from first principles". In this class we shall study:

- what are the 1-st principles?
- what approximations do we make?
  Ab initio = an art of approximation.

- how to balance accuracy vs cost?

Today there are many packaged programs allowing to perform wide range of electronic structure calculations, e.g., Q-Chem, Gaussian, GAMESS, PSI, ACES III and C4 (former ACES II), Spartan, Jaguar, MOLPRO, MOLCAS. General problem is how to design calculations relevant to a particular problem. You can consult manuals and learn how to prepare a working input for these programs. By trying to run different calculations, you will learn about cost of calculations, for example, what kind of calculations you cannot afford for your system. However, you cannot learn from the manual, or from officially looking output of the program with many digits in energy what is an accuracy of your calculations, and whether this accuracy is sufficient for your specific problem. That is why we have to study theory of electronic structure calculations, namely, what are different approximation which we use, what are physical considerations behind them, and what limitations they impose. We shall also design and perform electronic structure calculations, and analyze their results.

Some general references: course textbook,[1] advanced texts,[2,3] prerequisites.[4] Reviews on modern electronic structure theory,[5,6] http://nobelprizes.com/nobel/nobel.html

1.1 Energy units

In electronic structure calculations we use atomic units. They are defined such that electron charge, electron mass, and Plank constant equal unity: e=1 (electron charge) & $\hbar$=1 (Plank constant) & m=1 (electron mass). What are the advantages of the atomic units?

- Equations assume simpler form, e.g., the Schrödinger equation (SE) for the hydrogen atom in atomic units is:

  $$(-\frac{1}{2}\nabla_r^2 - \frac{1}{2M}\nabla_R^2 - \frac{1}{|R-r|})\Psi(r,R) = E\Psi(r,R) \tag{1.1}$$

  as compared to the SE in the SI units:

  $$(-\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_R^2 - \frac{e^2}{4\pi\epsilon_0|R-r|})\Psi(r,R) = E\Psi(r,R) \tag{1.2}$$

- The results do not depend on accuracy to which the universal constants are known, e.g., e, m_e and $\hbar$. These constants have being permanently refined, and atomic units allow for comparing the results of calculations performed 30 years ago and today. In order to compare the results of calculations presented in SI units, one has to account for different numerical values of the universal constants being used in the calculations.

In Szabo book, on page 42 you can find the conversion table of the atomic units to the SI units. Some important units to remember are listed in Table 1.1.

Table 1.1: Atomic units: Important constants to remember.

Quantity	Atomic units	Value
Length	a_o, or bohr	0.52918 Å
Dipole moment	2 unit charges separated by a_o	2.5418 Debyes (D)
Energy	hartree	27.211 eV
		627.51 kcal/mole
		$4.36 \cdot 10^{-18}$J
		$1.042 \cdot 10^{-18}$cal
		$2.195 \cdot 10^{5}$ cm^{-1}
		$6.58 \cdot 10^{15}$Hz
		$3.158 \cdot 10^{5}$ K

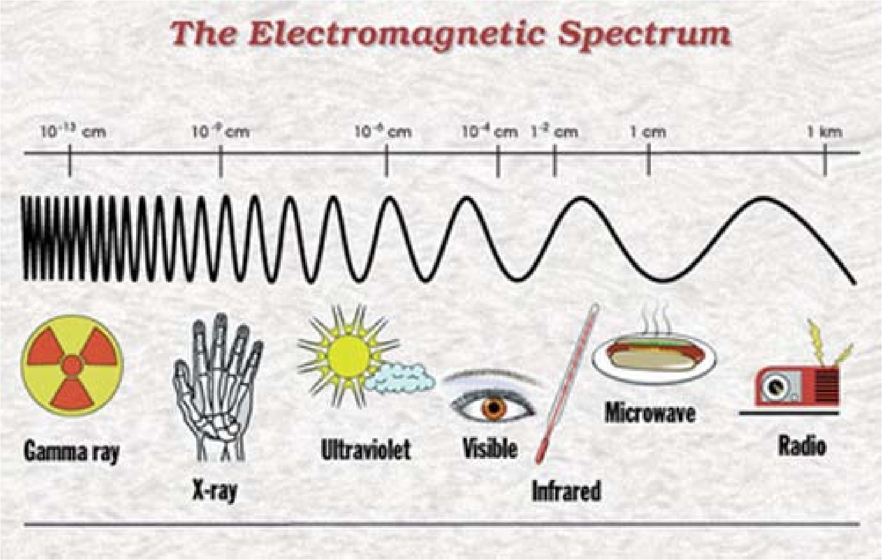


Figure 1.1: Energy range relevant to chemistry and chemical physics.

1.2 Energy range

Let us consider what energy range is of interest for physical chemistry (see Table 1.2 and Fig. 1.1).

Here (and always) we are interested in energy differences, e.g., vibrational spectroscopy measures energy spacings between vibrational levels, and so on. However, it is important to understand how these *relative energies* are related to the *total* energy of the chemical system.

Energy of the hydrogen atom is -0.5 hartree, energy of the ethylene molecule is about -80 hartree, energy of hexatriene is already couple of hundreds hartree. That is one of the reasons why electronic structure calculations are so challenging: in order to address chemical problems we need to achieve an incredible accuracy in relative energetics relative to the total energy. For example, an error of one percent in total energy for the ethylene equals 8 hartree. If this error is not uniform upon

Table 1.2: Energy ranges.

Process	Energy, hartree	Experiment
Annihilation	10^4	elementary particles' physics
Radioactivity	10^2	Messbauer, synchrotron, gamma-electron spectroscopies
	1	photoelectron spectroscopy
Ionization, electronic excitation, dissociation (bond energy)	0.1-0.01	Electronic spectroscopy chemistry
Molecular vibrations	10^{-2}-10^{-3}	IR, Raman
Molecular rotations	10^{-4}-10^{-6}	Far IR, radiofrequencies
Spin	$< 10^{-4}$	NMR, EPR
Orientation in molecular solids		ultrasound

geometry changes, it can give the same error in vibrational levels, which means that the error would be 3 orders of magnitude larger than calculated quantity! That is why electronic structure calculation is an art of making balanced approximations which result in error cancellation.

1.3 Adiabatic approximation

1.3.1 Potential energy surfaces and the electronic Hamiltonian

We start from the non-relativistic Schrödinger equation (SE) for the system of n electrons and N nuclei. Exact many electron, many nuclei problem is described by the following SE:

$$H\Psi_i(r,R) = E_i\Psi_i(r,R), \tag{1.3}$$

where $r = r_1, r_2, \ldots, r_n$, $R = R_1, R_2, \ldots, R_N$ represent the electron and nuclear coordinates, respectively, and

$$H = T_e + T_n + V_{en} + V_{ee} + V_{nn} \tag{1.4}$$

The kinetic energy terms are:

$$T_e = -\sum_i^n \frac{p_i^2}{2} \qquad \& \qquad T_n = -\sum_A^N \frac{P_A^2}{2M_A}, \tag{1.5}$$

where $p^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 = \Delta$.

The Coulomb terms are:

$$V_{ee} = \frac{1}{2}\sum_{ij}^n \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \quad \& \quad V_{nn} = \frac{1}{2}\sum_{AB}^N \frac{Z_A Z_B}{|\boldsymbol{R}_A - \boldsymbol{R}_B|} \quad \& \quad V_{en} = -\sum_i^n\sum_A^N \frac{Z_A}{|\boldsymbol{r}_i - \boldsymbol{R}_A|} \tag{1.6}$$

The solution of equation (1.3) yields wave functions that depend on the coordinates of all nuclei and all electrons. Intuitively, we feel that nuclear and electronic motions are very different, because their masses are very different, e.g., the proton mass is 3 orders of magnitude larger than the electron mass. If the masses of nuclei were infinite, equation (1.3) would reduce to the equation for interacting electrons moving in the potential of fixed nuclei. Each nuclear configuration would produce different external potential, which means that electronic energies/wavefunction would depend on nuclear positions parametrically. We cannot, however, just set up $M = \infty$ (i.e., $T_N = 0$), since then we would not be able to describe nuclear dynamics (there would be no dynamics!). But since the nuclear motion is much slower relative to electronic motion, we can expect that electrons can adjust almost simultaneously to any new position of nuclei. Let us see how we can separate nuclear and electronic motion.

Let us define so-called electronic wavefunctions to be solutions of the electronic SE:

$$H_{el}\Phi_i(r;R) = U_i(R)\Phi_i(r;R) \tag{1.7}$$

$$H_{el} \equiv T_e + V_{en} + V_{ee} + V_{nn} \tag{1.8}$$

We can solve this equation at each fixed geometry of nuclei, and resulting solution (U and Φ) will depend *parametrically* on nuclear geometry (we use ';' instead of ',' to distinguish between parametric and explicit dependence on R). Calculated adiabatic potential energy curves $U_i(R)$ of O_2 molecule are shown in Fig. 1.2. We will see later that $U(R)$ is a potential which governs nuclear motion (bound states — vibrational motion, unbound states — dissociation, etc). At each internuclear distance, the lowest energy solution of the electronic SE gives ground state energy. Higher energy solutions describe electronically excited states. Note that some of the states are unbound, i.e., if molecule is excited to one of such states, it dissociates to two oxygen atoms.

Equation (1.8) is the equation of the electronic structure theory. This is what we solve and this is our "first principle".

Now we want to express solutions of full problem (1.3) in terms of the solutions of the electronic problem. We can express the exact wavefunction Ψ as:

$$\Psi_i(r,R) = \sum_j \Phi_j(r;R)\xi_j^i(R) \tag{1.9}$$

Here functions Φ_j are used as a basis, and so called nuclear functions $\xi_j^i(R)$ are expansion coefficients to be determined. From now on, we will skip r, R, we will just remember that $\Phi_j \equiv \Phi_j(r;R)$ and $\xi_j^i \equiv \xi_j^i(R)$.

Now we want to derive equations for so defined ξ_j^i. Substitute ansatz (1.9) into SE (1.3):

$$(H_{el} + T_N)\sum_j \Phi_j\xi_j^i = E_i\sum_j \Phi_j\xi_j^i \tag{1.10}$$

Multiply this equation by Φ_k on the left, and integrate over the electronic coordinates:

$$\sum_j < \Phi_k|H_{el}|\Phi_j >_r \xi_j^i + \sum_j < \Phi_k|T_N|\Phi_j\xi_j^i >_r = E_i\sum_j < \Phi_k|\Phi_j >_r \xi_j^i \tag{1.11}$$

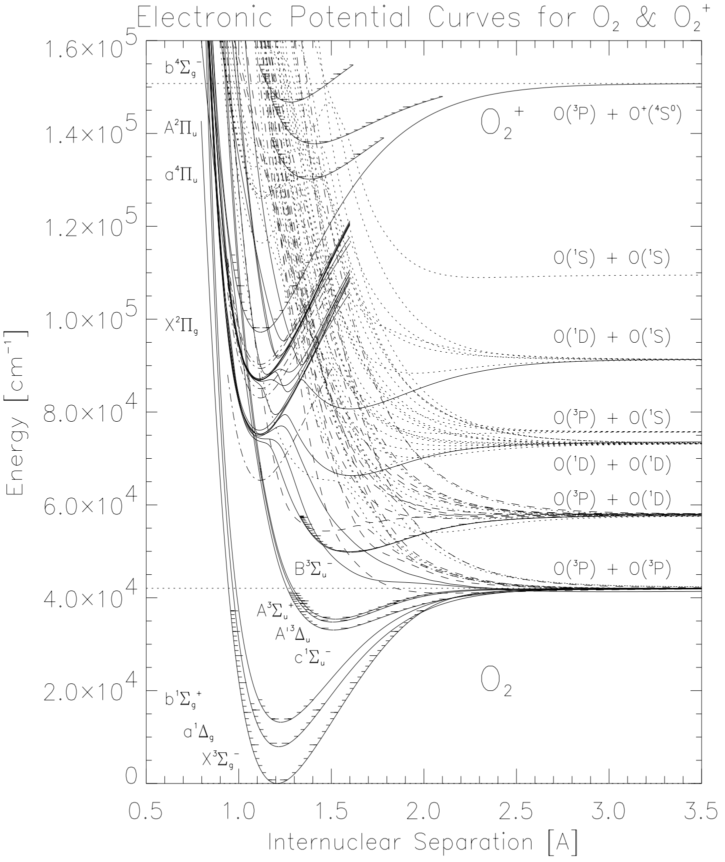


Figure 1.2: Calculated adiabatic potential energy curves of O_2 molecule. At each internuclear distance, the lowest energy solution of the electronic SE gives ground state energy. Higher energy solutions describe electronically excited states. Note that some of the states are unbound, i.e., if molecule is excited to one of such states, it dissociates to two oxygen atoms. Reproduced from Morill *et al.*, *Review of electronic structure of molecular oxygen*, a web report published on the NIST website.

Let us analyze Eq. (1.11) term-by-term:

$$\sum_j < \Phi_k|H_{el}|\Phi_j >_r \xi_j^i = U_k(R)\xi_k^i \tag{1.12}$$

$$\sum_j < \Phi_k|\Phi_j >_r \xi_j^i = \xi_k^i \tag{1.13}$$

in virtue of Eq. (1.8) and the orthonormality of the electronic functions Φ_j. The kinetic energy term:

$$\begin{aligned} -\sum_j < \Phi_k|T_N|\Phi_j\xi_j^i >_r \equiv \sum_A\sum_j \frac{1}{2M_A} < \Phi_k|\nabla_A\nabla_A|\Phi_j\xi_j^i >_r = \\ \sum_A\sum_j \frac{1}{2M_A} < \Phi_k|\nabla_A\{(\nabla_A\Phi_j)\xi_j^i + \Phi_j\nabla_A\xi_j^i\} >_r = \\ \sum_A\sum_j \frac{1}{2M_A} < \Phi_k|\{(\nabla_A^2\Phi_j)\xi_j^i + \nabla_A\Phi_j\nabla_A\xi_j^i + \nabla_A\Phi_j\nabla_A\xi_j^i + \Phi_j\nabla_A^2\xi_j^i\} >_r = \\ \sum_A \frac{1}{2M_A}\left(\sum_j < \Phi_k|\nabla_A^2\Phi_j >_r \xi_j^i + 2\sum_j < \Phi_k|\nabla_A\Phi_j >_r \nabla_A\xi_j^i + \nabla_A^2\xi_k^i\right) \end{aligned} \tag{1.14}$$

Therefore we end up with the following set of equations for ξ_j^i:

$$(T_N + U_k(R) - E_i)\,\xi_k^i = \sum_A \frac{1}{2M_A}\left(\sum_j < \Phi_k|\nabla_A^2\Phi_j >_r \xi_j^i + 2\sum_j < \Phi_k|\nabla_A\Phi_j >_r \nabla_A\xi_j^i\right) \tag{1.15}$$

If we could neglect terms on the right, we would end up with an eigenproblem for nuclei moving in the potential U_k, which is mean field potential of electrons (electron cloud). For each U_k we can find nuclear eigenstates, and eigenstates for different U_k are independent. In this case ansatz (1.9) assumes simpler form:

$$\Psi_{ik} = \Phi_i\xi_k^i \tag{1.16}$$

We can consider PES's from Fig. 1.2. For bound states, there will be quantized vibrational energy levels, and localized nuclear vibrational wavefunctions (similar to harmonic oscillator functions). Solution of the nuclear SE for unbound PES's will produce continuum energy levels and wave-like wavefunctions.

In the classical limit, we can consider nuclei as spheres moving on the given potential U_k. Once nuclei are placed on the given U_k, they will stay on this surface forever: electronic state U_k cannot change to U_i upon nuclear motion. In other words, electrons can adjust to a new nuclear position simultaneously. They are infinitely fast relative to nuclei. This is adiabatic (Born-Oppenheimer approximation).

Let us analyze terms on the right. What do they do? Consider their diagonal part. Some correction to the energy, second is zero. Non-diagonal parts: they couple nuclear dynamics on different electronic states. Using classical language, due to this terms electronic state can change upon the nuclear motion — there is a probability of non-adiabatic hops. When these terms can be large? When electronic wavefunction depend strongly on nuclear geometry (derivative terms)! Fig. 1.3 shows adiabatic PES's for NaI. At equilibrium, the molecule is ionic. However, lowest energy gas phase dissociation channel is neutral one. Thus, the wavefunction changes its character from ionic to neutral, and the derivative coupling may be large. It is possible to consider so called diabatic states, states that do not change their nature as a function of nuclear geometry. These states are no longer eigenstates of electronic SE. Thus, they are coupled by a *potential coupling*, an off-diagonal matrix element of the Hamiltonian in the basis of diabatic states.

Term $< \Phi_k|\nabla_A^2\Phi_j >_r \xi_j^i$ is just some potential coupling (acts as additional potential for nuclei). To be important, it has to be large relative to diagonal parts of the Hamiltonian (potential U_k). So its importance is defined solely by the value of the integral $< \Phi_k|\nabla_A^2\Phi_j >_r$ and the potentials U_k. Term $\sum_j < \Phi_k|\nabla_A\Phi_j >_r \nabla_A\xi_j^i$, however, is different. It has two parts: integral $\sum_j < \Phi_k|\nabla_A\Phi_j >_r$, and nuclear momentum $\nabla_A\xi_j^i$. Therefore, this term can become very large when nuclear velocity is high. Here we can discuss two limits: adiabatic limit: nuclei are very slow, electrons follow nuclear motion and adjust to it. Nuclear are very fast — electrons cannot adjust to nuclear motion — non-adiabatic "hops".

As a homework, use PT to analyze term $\sum_j < \Phi_k|\nabla_A\Phi_j >_r$ to understand when it can be large (see Fig. 1.4).

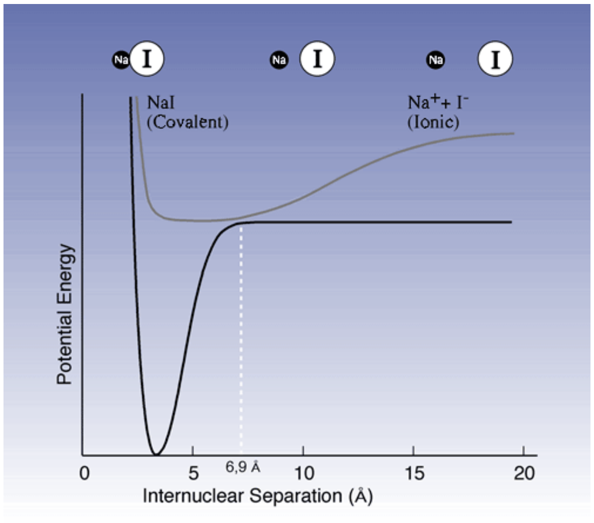


Figure 1.3: Adiabatic states change their character from ionic to covalent (and vice-verse) upon dissociation, and thus interact strongly through the derivative coupling. Two diabatic states preserve the purely ionic or covalent character. These are coupled by non-derivative, i.e., potential, coupling, an off-diagonal matrix element of the Hamiltonian in the basis of diabatic states.

1.3.2 Non-Adiabatic Dynamics: An example

Consider photodissociation of bromacetil chloride (Br-CH_2COCl).[7] As summarized in Fig. 1.5, once the molecule is photoexcited (with sufficient energy) into S_1 state, there are two channels open for photodissociation: C-Br bond fission and C-Cl bond fission. The barrier for C-Br bond breaking channel is 10 kcal/mol lower than the C-Cl one, however, the branching ratio is 0.4:1.0 (in favor of the latter). Why? Non-adiabatic re-crossing — the NA couplings are much stronger for the C-Br channel, thus diabatic dynamics, repulsive wall, etc.

1.3.3 Adiabatic approximation: Summary

1. Electronic problem gives PES for ground and excited states.

2. Nuclear dynamics: Nuclear motion on BO surface (bound, unbound levels). Vibrations and rotations.

3. When Born-Oppenheimer approximation is valid?

4. What can happen when BO breaks?

5. How to solve the full problem (using Ψ_{el} as a basis) ?

1.3.4 Potential energy surfaces: concepts and definitions

Consider a solution of electronic Schrödinger equation: $E(R) \equiv U(R)$. $E(R)$ defines nuclear motion (in adiabatic approximation) and is called potential energy surface (PES).

Gradient (vector): $grad_R = \nabla_R = \frac{\partial}{\partial R_1}, \ldots, \frac{\partial}{\partial R_{3n}}$

Hessian (matrix): $H_{R_i,R_j} = \nabla_{R_i}\nabla_{R_j} = \frac{\partial^2}{\partial R_i \partial R_j}$

Stationary points of PES $\equiv$ gradient vanishes in all directions: $\frac{\partial E}{\partial R_i} = 0$

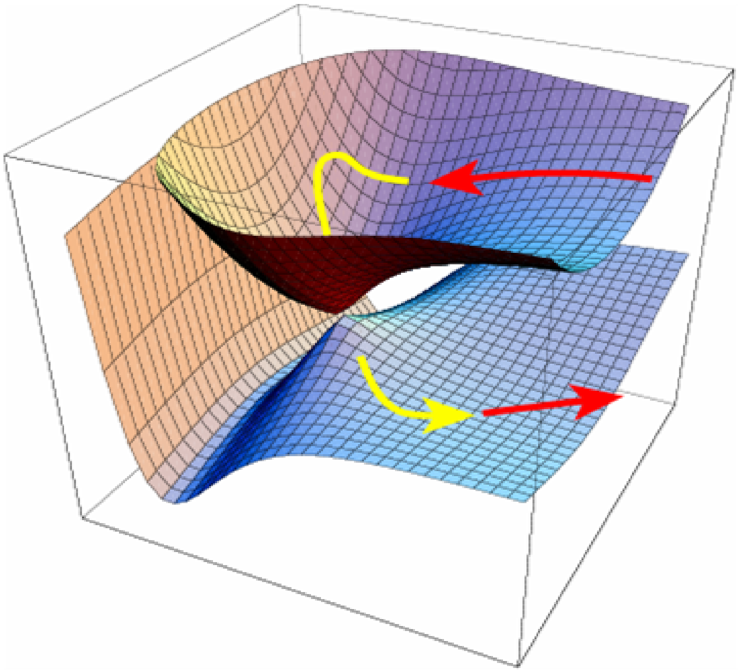


Figure 1.4: The derivative coupling becomes large when PESs approach each other. The probability of non-adiabatic transitions are significant around so-called *conical intersections.*

- minimum (positive curvature in all directions, $\frac{\partial^2 E}{\partial R_i \partial R_j} > 0$) — stable molecular structures
- maximum (negative curvature in all directions, $\frac{\partial^2 E}{\partial R_i \partial R_j} < 0$)
- saddle point of order m (negative curvature in only m directions, matrix $\frac{\partial^2 E}{\partial R_i \partial R_j}$ has m negative roots) — transition structures connecting minima

Figs. 1.6,1.7 show PESs for the dissociation of cyclobutane to two ethylene molecules. Note minima corresponding to stable products and transition states. Minima are connected through transition states. Barriers define reaction rates.

Figs. 1.8-1.10 show PES's for HNCO. Number of internal degrees of freedom: 3N-6, N=4. 6 internal degrees of freedom: R_{HN}, R_{NC}, R_{CO}, α_{HNC}, α_{NCO}, and torsion angle (deviation from planarity). Fig. 1.8 is one dimensional diagram along minimal energy paths connecting different isomers, e.g., HCNO and HOCN. Fig. 1.9 is a 2D contour plot, $E(R_{HN},\alpha_{NCO})$, all other degrees of freedom being frozen. There are two stable minima connected by transition state (saddle point), and a valley along dissociation coordinate (also separated by transition states from the stable isomers). Fig. 1.10, $E(R_{HN},R_{NC})$, shows two dissociation channels.

1.4 Approximation in electronic problem

From now on, we shall use the following notations:

$$H \equiv H_{el} \quad \& \quad \Psi \equiv \Phi_{el}(r;R) \tag{1.17}$$

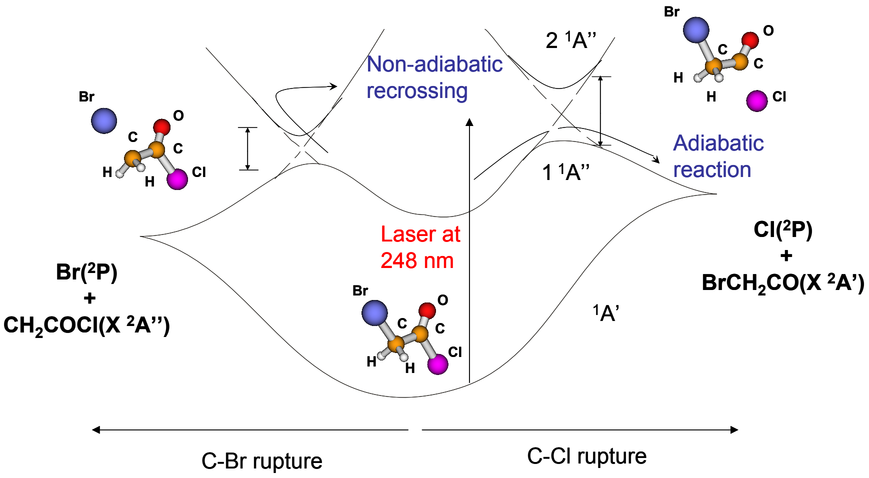


Figure 1.5: Two competing channels found in the photodissociation of $\mathrm{Br(CH_2)}_n\mathrm{COCl}$. Following photoabsorption, the molecule on the upper electronic surface can dissociate along any of two bonds, either C-Cl or C-Br. In spite of the higher adiabatic barrier in the first channel (0.4 eV difference), the actual branching ratio 1:0.4 is in favor of this reaction. The reason is that the second reaction is strongly non-adiabatic, such that the molecule fails to switch its initial bonding electronic configuration to the antibonding one of the fragmentation products. As a result, the molecule rebounces from the potential wall and recrosses back to the region of reagents even though it has enough energy to surmount the adiabatic barrier. Conversely, the C-Cl bond cleavage does successfully proceed via the adiabatic route. Figure courtesy of Rosendo Valero and Don Truhlar.

Why cannot we solve electronic problem exactly?
$H\Psi = E\Psi$, a differential equation in many coordinates, is not directly available for computer solution →
we must convert it to algebraic equation because we'd like to solve for numbers (expansion coefficients) rather than functions →
$\Psi = \sum_i c_i \Phi_i$, where c_i are expansion coefficients and $\{\Phi_i\}$ — set of many-electron expansion functions.

What are they?

1.4.1 A valid many-electron function

A valid many-electron function must be single-valued, continuous, and normalized:

$$< \Psi|\Psi >= \int_{-\infty}^{+\infty} \Psi^*(\boldsymbol{x})\Psi(\boldsymbol{x})d\boldsymbol{x} \tag{1.18}$$

It also should posses certain symmetries, i.e.:

- Permutational symmetry (electrons are indistinguishable, so nothing should change if we swap two electrons).

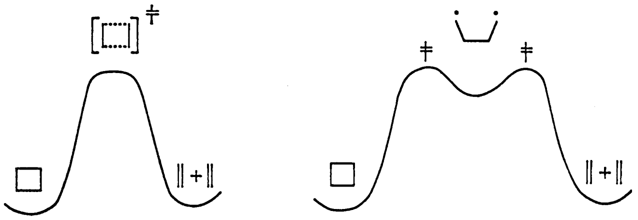


Figure 1.6: Schematic depiction of two possible pathways for ring opening in cyclobutane. The two diagrams depict the transition state and diradical mechanisms, respectively. Reproduced from S. Pedersen, J.L. Herek, and A.H. Zewail, *The validity of the "diradical" hypothesis: Direct femtosecond studies of the transition-state structures*, Science **266**, 1359 (1994).

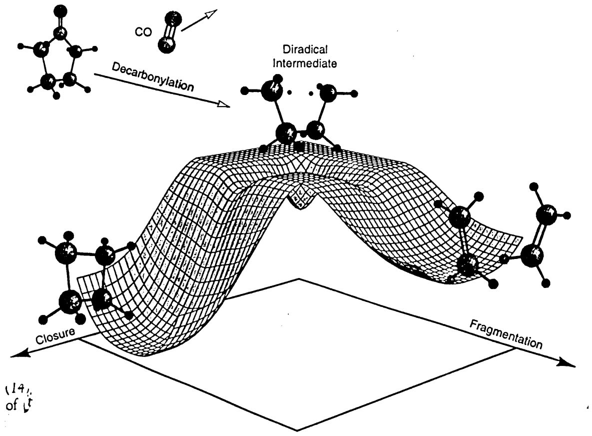


Figure 1.7: Schematic depiction of the diradical reaction for ring opening in cyclobutane. Extrusion of the carbon monoxide group from the parent molecule can create a diradical (tetramethylene), if the dissociation is followed shortly by a radiationless transition to the ground electronic state. Shown are the two channels for product formation, closure of cyclobutane or fragmentation to two ethylene molecules. Reproduced from S. Pedersen, J.L. Herek, and A.H. Zewail, *The validity of the "diradical" hypothesis: Direct femtosecond studies of the transition-state structures*, Science **266**, 1359 (1994).

- Spatial symmetry defined by the point group symmetry of the external potential, i.e., nuclei. For example, consider H_2 molecule: nothing should change if we swap nuclei.

- Be an eigenfunction of spin-operators $\hat{S}_z$ and $\hat{S}^2$.

In all of the above, we used the following result from Quantum Mechanics: if a certain operator $\hat{A}$ commutes with the Hamiltonian, i.e., if:

$$\left[\hat{H}, \hat{A}\right] = 0, \tag{1.19}$$

$\hat{H}$ and $\hat{A}$ have common eigenfunctions (eigenfunctions of $\hat{H}$ are also eigenfunctions of $\hat{A}$).

We shall discuss and use all of the above symmetries. Today we will talk only about permutational symmetry, i.e., the Pauli principle.

Consider a system of indistinguishable particles, e.g., electrons of nuclei. $[H, P] = 0$, where P — permutation operator → H,P have common eigenfunctions.

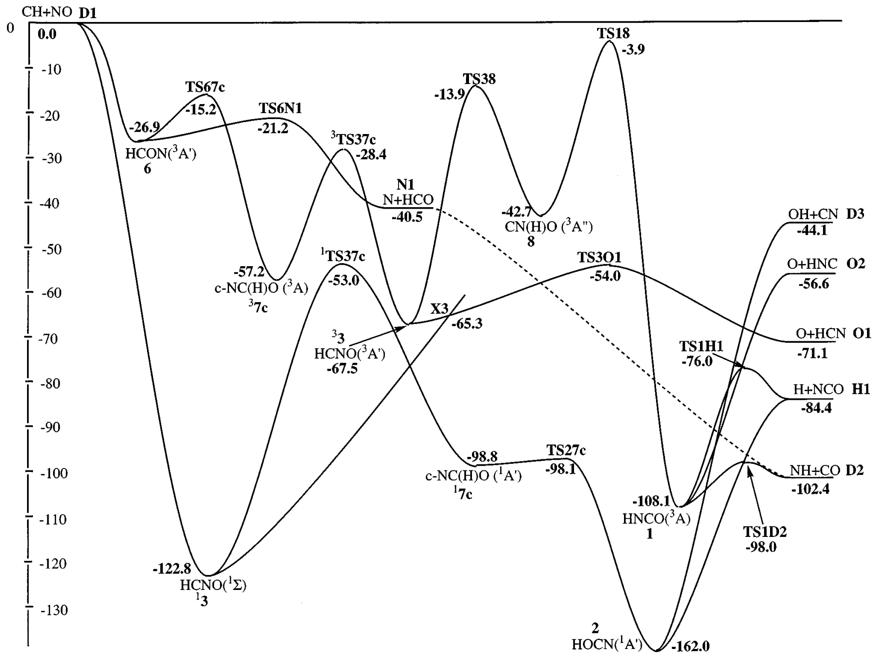


Figure 1.8: Profile of PES for the CH($^2\Pi$)+NO($^2\Pi$) reaction. Note different isomers and transition states. Reproduced from: A.M. Mebel, A. Luna, M.C. Lin, and K. Morokuma, *A density functional study of the global potential energy surfaces of the [H,C,N,O] system in singlet and triplet states*, J. Chem. Phys. **105**, 6439 (1996).

Consider P_{12} for 2-particle system:

$$\begin{aligned} P_{12}\Psi_{12} &= \lambda\Psi_{12} \\ P_{12}P_{12}\Psi_{12} = \Psi_{12} &= \lambda^2\Psi_{12} \rightarrow \\ \lambda^2 = 1 &\rightarrow \lambda = \pm 1 \end{aligned} \tag{1.20}$$

Bosons: $P_{12}\Psi_{12} = \Psi_{12}$ (symmetric w.f.).
Fermions: $P_{12}\Psi_{12} = -\Psi_{12}$ (antisymmetric w.f.).

Naturally, in this class we are concerned about *fermions* and *antisymmetric* wave functions. What would be a simple and convenient *ansatz* for such a wave function? A determinant composed of one-electron functions (orbitals, or, more precisely, spin-orbitals).

Consider 2-electron system, e.g., He atom. Let us take the following ansatz:

$$\Psi(1,2) = \phi_1(1)\phi_2(2), \tag{1.21}$$

where $\phi(1)$ is some one-electron function, e.g., a wave function for He$^+$ system (e.g., $\phi_1 = 1s\alpha$ and $\phi_2 = 1s\beta$). In order to make the wave function (1.21) a valid one, we have to anti symmetrize it:

$$P_{12}\Psi(1,2) = P_{12}\phi_1(1)\phi_2(2) = -\phi_1(2)\phi_2(1) \neq -\Psi(1,2) \tag{1.22}$$

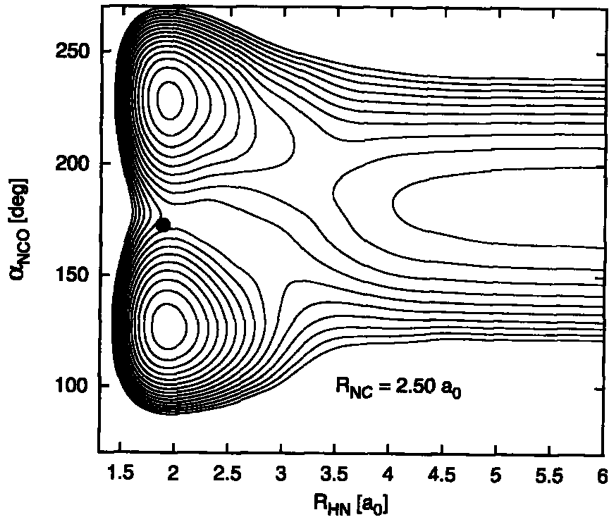


Figure 1.9: Two-dimensional cut through the PES of excited $^1S_1$ state of HNCO. The heavy dot marks the Franck-Condon point. Reproduced from: J.-J. Klossika, H. Flöthmann, C. Beck, R. Schinke, K. Yamashita, *The topography of the HNCO (S_1) potential energy surface and its implications for photodissociation dynamics*, Chem. Phys. Lett. **276** 325 (1997).

However,

$$\begin{aligned} P_{12}\left[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)\right] &= \phi_1(2)\phi_2(1) - \phi_1(2)\phi_2(1) = \\ &- \left[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)\right] = -\Psi(1,2) \end{aligned} \tag{1.23}$$

The above (anti-symmetrized) wave function can be compactly written as a determinant:

$$\Psi(1,2) = det(\phi_1\phi_2) = \begin{pmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{pmatrix} \tag{1.24}$$

We should, of course, worry about proper normalization, but this is easy. For the system of n electrons, the normalization coefficient is $\frac{1}{\sqrt{n!}}$ given that one-electron functions are normalized to one.

Thus, the simplest n-electron antisymmetric functions: determinant composed of n different 1-electron functions:

$$\begin{aligned} |\Psi(x_1x_2\ldots x_n)> &= \frac{1}{\sqrt{n!}} det\{\phi_1\phi_2\ldots\phi_n\} = \\ \frac{1}{\sqrt{n!}} &\begin{pmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_n(2) \\ \ldots & & & \\ \phi_1(n) & \phi_2(n) & \ldots & \phi_n(n) \end{pmatrix} \end{aligned} \tag{1.25}$$

Note that electron labels include not only the coordinates of the electrons, $\boldsymbol{r}_i$, but also spin, $\boldsymbol{s}_i$. Thus we call the one-electron functions “spin-orbitals”.

1.4.2 Towards the exact solution

If we are given a set of M spin-orbitals, then

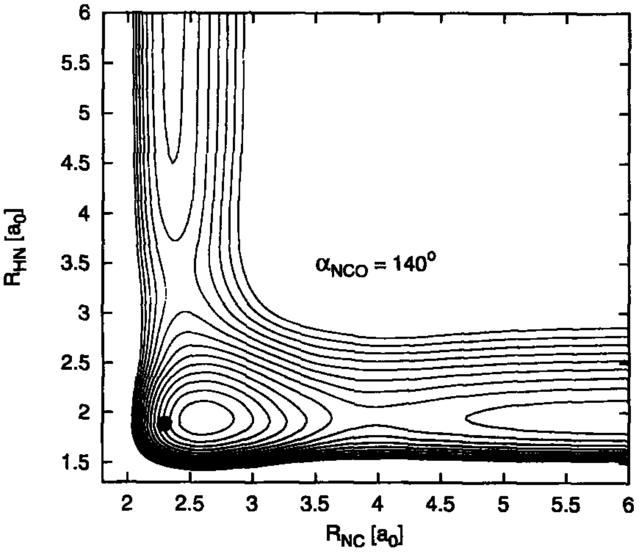


Figure 1.10: Two-dimensional cut through the PES of the excited $^1S_1$ state of HNCO. The heavy dot marks the Franck-Condon point. Reproduced from: J.-J. Klossika, H. Flöthmann, C. Beck, R. Schinke, K. Yamashita, *The topography of the HNCO (S_1) potential energy surface and its implications for photodissociation dynamics*, Chem. Phys. Lett. **276** 325 (1997).

- The best solution we can obtain to an N-electron problem will be to combine together all valid determinants:

$$\Psi = \sum_i c_i \Phi_i \tag{1.26}$$

  and use the variational principle to minimize E.

- If those M spin-orbitals are flexible enough to describe any 1-electron function ("completeness") then this will yield the exact solution!

Full Configurational Interaction (FCI) is what we have just described.

FCI is exact solution of electronic Schrödinger equation in a given spin-orbital basis.

How many configurations? It is the number of ways we can draw N different spin-orbitals from a pool of M, in a unique fashion:

$$\#configurations = C_M^N = \frac{M!}{N!(M-N)!} \tag{1.27}$$

A relatively harmless-looking expression, but devastating in practice. Consider that both N & M are proportional to the size of molecule

Exponential growth: $C_M^N \approx 10^N$

Let us see what does it mean in terms of molecules:

Today's largest FCI calculations:[8] methylene, CH_2, in TZ2P basis, with core-orbital frozen. Basis set is large enough to give accurate results, but is still far from being complete, e.g., errors in excitation energies are ≈ 0.04 eV.

1.4.3 The notion of a theoretical model chemistry

We have reviewed how to solve the electronic problem exactly, and have declared it unfeasible, at least in general:

Table 1.3: Number of configuration for the M/N=5

N	M	C_M^N
2	10	45
4	20	4845
6	30	593775
8	40	$7.7*10^7$
10	50	$1.0*10^{10}$
20	100	$5.4*10^{20}$

Table 1.4: Number of electrons, N, in some simple molecules

$Molecule$	N
H_2O	10
C_2H_4	16
C_4H_8	32

- for a fixed ratio $N : M$, we observe exponential growth in the number of configurations;
- to obtain completeness, M must become very large

There are hence two fundamental approximation that will be usually made in quantum chemistry:

- we find some way of reducing the number of configurations involved in wave function:

  "we do not solve the exact equations"

  "approximate treatments of electron-electron interactions, or electron correlation"

- We do not achieve completeness in the one-particle expansion space

  "we do not solve inexact equation exactly"

  "basis set truncation error"

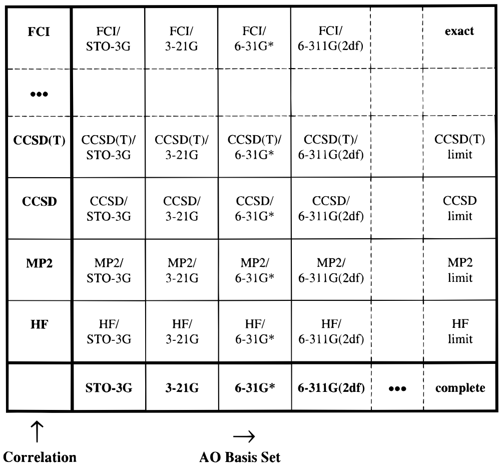
These two approximations may be nicely summarized on a chart — first introduced by Pople in 1965 — a two-dimensional chart of quantum chemistry (see Fig. 1.11).

The one-configurational model is Hartree-Fock theory, the smallest feasible basis set is termed "minimal", both these concepts will be discussed in details later.

A given entry on this chart defines a "theoretical model chemistry", a model of reality which can be used to make comparisons with experiment and predictions.[9]

To solve a given problem using electronic structure theory involves the selection of a theoretical model which is

- feasible when applied to the problem
- sufficiently accurate that meaningful results are obtained



FCI	FCI/ STO-3G	FCI/ 3-21G	FCI/ 6-31G*	FCI/ 6-311G(2df)		**exact**
•••						
CCSD(T)	CCSD(T)/ STO-3G	CCSD(T)/ 3-21G	CCSD(T)/ 6-31G*	CCSD(T)/ 6-311G(2df)		CCSD(T) limit
CCSD	CCSD/ STO-3G	CCSD/ 3-21G	CCSD/ 6-31G*	CCSD/ 6-311G(2df)		CCSD limit
MP2	MP2/ STO-3G	MP2/ 3-21G	MP2/ 6-31G*	MP2/ 6-311G(2df)		MP2 limit
HF	HF/ STO-3G	HF/ 3-21G	HF/ 6-31G*	HF/ 6-311G(2df)		HF limit
	STO-3G	**3-21G**	**6-31G***	**6-311G(2df)**	•••	**complete**

Figure 1.11: Two-dimensional chart of quantum chemistry. A theoretical model chemistry is defined by the two main approximations that are made in order to make solution of the Schrödinger equation tractable.These are the level of correlation treatment and the extent of completeness of the set of basis functions which are used to represent molecular orbitals. The chart arranges approximations in order of increasing accuracy along the two axe, so that model chemistries toward the top right approach exact solution of the Schrödinger equation (FCI in the complete basis set). The horizontal axis contains a series of (one-particle) basis sets of increasing complexity (minimal, double zeta, double-zeta plus polarization, etc). The vertical axis contains a series of increasingly sophisticated models of electron correlation. Reproduced from M. Head-Gordon, J. Phys.Chem. **100**, 13213 (1996).

Balancing these 2 factors is what I want you to get out of this course.

Before we begin our studies of different theoretical model chemistries it is useful to consider additional attributes that they should possess. These may seem obvious, but we shall find it is hard to satisfy them all.

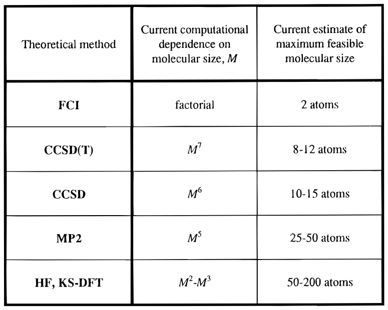
1. feasibility (scaling & timing)
2. accuracy (error bars)
3. predictive
4. size-consistent (“size-extensive”)
5. variational

Scaling: how does cost of calculations increase with molecular size increase. Timing: how much time does it take for a particular system. See Fig. 1.12.

Predictive: no experimental input, or molecule-specific data beyond nuclear positions, electron number, and state multiplicity should be required: “Electrons & nuclei in, energies out”. A model chemistry meeting this criterion can be applied in an unambiguous fashion to any molecule. Black-box tool.

Size-consistency (“size-extensivity”): The energy of a set of identical noninteracting molecules should be proportional to their number. Again, obvious to state, because without this property we cannot reliably compare molecules of different sizes (e.g., we cannot look at processes which involve fusing or fragmenting molecules). But many common approximations are not size-consistent).

Variationality: “upper bound to the energy”.



Theoretical method	Current computational dependence on molecular size, M	Current estimate of maximum feasible molecular size
FCI	factorial	2 atoms
CCSD(T)	M^7	8-12 atoms
CCSD	M^6	10-15 atoms
MP2	M^5	25-50 atoms
HF, KS-DFT	M^2-M^3	50-200 atoms

Figure 1.12: Scalings of electronic structure theory methods with molecular size, M, and estimates of the maximum molecular sizes (in terms of numbers of first-row non-hydrogen atoms) for which energy and gradient evaluations can be tackled by each method at present (e.g., in 1996). The latter estimates are very approximate because they depend critically on many variables beyond simply the size dependence of computational complexity and the assumed availability of a high-end workstation. Other factors include the number of energy and gradient evaluations required (assumed to be fewer than 10), the size of the basis set chosen (assumed to be DZP quality), molecular symmetry (none assumed), etc. Typical current calculations are of course on substantially smaller molecules at each level of theory. Nevertheless, the overall pattern of steep reduction in maximum feasible molecular size with increasingly sophisticated electron correlation treatments is an accurate reflection of the current limits of electronic structure models. It also illustrates the need for new algorithms which scale more physically with molecular size. Reproduced from M. Head-Gordon, J. Phys.Chem. **100**, 13213 (1996).

1.5 Calibration of electronic structure models

How to characterize accuracy of electronic structure calculations? We do not attempt to obtain truly converged results for each specific molecule but rather are interested in black-box methods which are not exact, but whose errors we can estimate. Therefore, it is very important to know what are intrinsic errors of approximate methods, i.e., theoretical model chemistry (see Fig. 1.13). An apparent error of a theoretical model chemistry (total error w.r.t. experiment) consists of the (one-particle basis) set error and the N-electron error (correlation approximation). The error of a method in the complete basis set limit is method's intrinsic error.

Statistics is essential! We adopt somewhat experimental approach: Let us study a large set of molecules, and statistically analyze errors of different methods — from these results we will see what kind of errors one can expect from a given model.

Today, we will discuss calibration results with respect to molecular equilibrium structures. This is the easiest (for *ab initio*) part — frequencies, reaction energies, excited states are more challenging. Calibration results can be found in Refs.[3, 10, 11]

1.5.1 Benchmarks: computational details

The set of 19 *closed-shell* molecules containing *first-row* atoms have been used for calibration of electronic structure methods w.r.t. equilibrium structures (see Fig 1.14). Note that the results do not necessarily carry over to open-shell molecules and

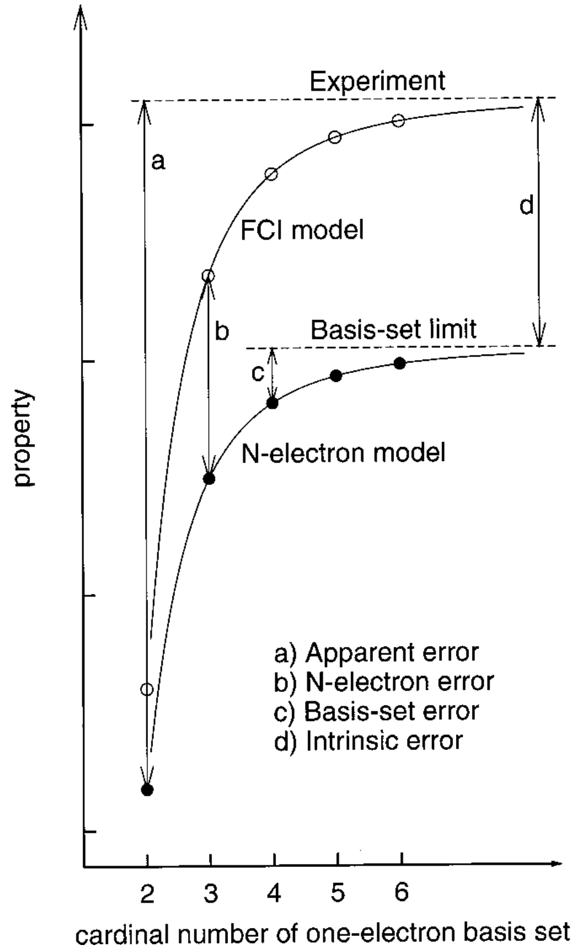


Figure 1.13: Schematic definition of the errors occurring in *ab initio* calculations with finite basis set and approximate N-electron wavefunctions. Reproduced from: Bak *et al.*, J. Chem. Phys. **112**, 9229 (2000).

molecules containing heavier elements. Moreover, we expect the performance to degrade in case of not so well-behaved closed-shell molecules, such as singlet diradicals, molecules away from equilibrium (e.g. at transition states), etc.

For the molecules from Fig. 1.14, the following hierarchy of approximate (N-electron) methods have been tested: Hartree-Fock, Møller-Plesset PT (MP2, MP3, and MP4), CCSD, and CCSD(T). CISD have also been included — it is instructive to compare this model vs. CCSD which is of approximately same complexity, but is a size-consistent method. For each approximate N-electron model, the series of one-particle basis sets of increasing complexity have been used to investigate the basis-set saturation effect (bases used for structures: cc-pVDZ, cc-pVTZ, cc-pVQZ).

1.5.2 Measures of errors

Let the calculated bond distances for a given method/basis set be denoted by R_i^{calc}, and let the corresponding experimental numbers be R_i^{exp}. The error is then given by:

$$\Delta_i = R_i^{calc} - R_i^{exp} \tag{1.28}$$

The following statistical measures of errors have been calculated: the mean error

HF, H_2O, NH_3, CH_4, N_2, CH_2, CO, HCN, CO_2, HNC, C_2H_2, CH_2O, HNO, N_2H_2, O_3, C_2H_4, F_2, HOF, H_2O_2

Figure 1.14: The 19 molecules (28 bond distances), on which the statistical analysis is based. Reproduced from: Helgaker *et al.*, J. Chem. Phys. **106**, 6430 (1997).

$\bar{\Delta}$, the standard deviation in the errors Δ_{std}, the mean absolute error $\bar{\Delta}_{abs}$, and the maximum error Δ_{max}:

$$\bar{\Delta} = \frac{1}{n}\sum_i^n \Delta_i \tag{1.29}$$

$$\Delta_{std} = \sqrt{\frac{1}{n-1}\sum_i^n (\Delta_i - \bar{\Delta})^2} \tag{1.30}$$

$$\bar{\Delta}_{abs} = \frac{1}{n}\sum_i^n |\Delta_i| \tag{1.31}$$

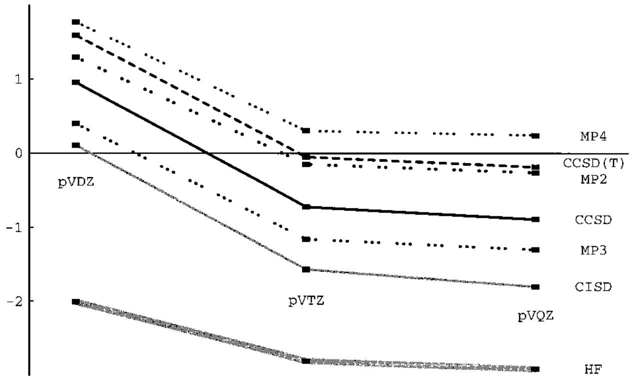
$$\Delta_{max} = max_i|\Delta_i| \tag{1.32}$$

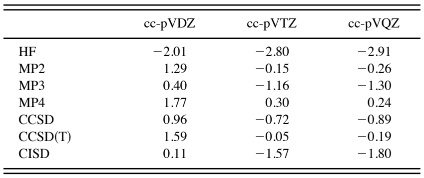
Each measure characterizes a specific aspect of the performance. The mean error and the standard deviation are most important — they show what the average error (remember about the sign!) is, and what is the width of the distribution. They quantify both systematic and non-systematic errors. What do we want the error distribution to be? A delta-like function centered at zero (zero error vs. experiment) — thus, both $\bar{\Delta}$ and Δ_{std} should be small for a reliable method. The mean absolute error represents the typical magnitude of the errors in calculations, and Δ_{max} gives the largest error.

Mean errors and standard deviations are shown in Figs. 1.15,1.16. Note that small mean errors can combined with large standard deviations (e.g., CISD in small basis sets). Another observation: mean error for MP2 is very similar to that of the CCSD(T), however the standard deviation of errors (in large basis sets) for these two methods is quite different. Basis set convergence: (i) basis set effects are larger for more correlated methods; and (ii) only CCSD(T) shows nice convergence towards very small Δ_{std}.

A more pictorial view is given in Fig. 1.17. Note that HF does not become more predictive in larger basis sets. CCSD(T) gives delta-like distribution in cc-pVTz basis set. MP2 is reasonably good, nice improvement over the Hartree-Fock model.

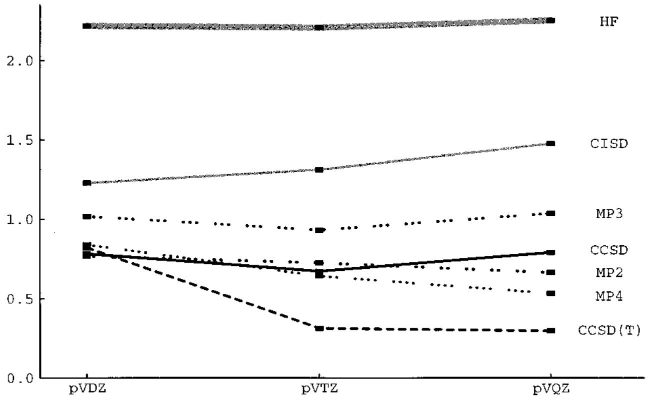
Mean absolute errors and maximum errors are shown in Figs. 1.18,1.19, respectively.

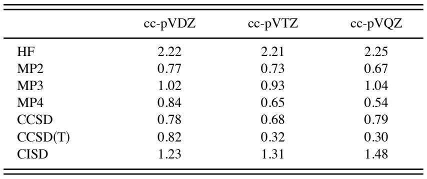




	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF	−2.01	−2.80	−2.91
MP2	1.29	−0.15	−0.26
MP3	0.40	−1.16	−1.30
MP4	1.77	0.30	0.24
CCSD	0.96	−0.72	−0.89
CCSD(T)	1.59	−0.05	−0.19
CISD	0.11	−1.57	−1.80

Figure 1.15: Mean errors $\bar{\Delta}$ relative to experiment in calculated bond distances, pm (10^{-12}m=0.01 Å). Reproduced from: Helgaker *et al.*, J. Chem. Phys. **106**, 6430 (1997).





	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF	2.22	2.21	2.25
MP2	0.77	0.73	0.67
MP3	1.02	0.93	1.04
MP4	0.84	0.65	0.54
CCSD	0.78	0.68	0.79
CCSD(T)	0.82	0.32	0.30
CISD	1.23	1.31	1.48

Figure 1.16: Standard deviations Δ_{std} in the errors relative to experiment in calculated bond distances, pm (10^{-12}m=0.01 Å). Reproduced from: Helgaker *et al.*, J. Chem. Phys. **106**, 6430 (1997).

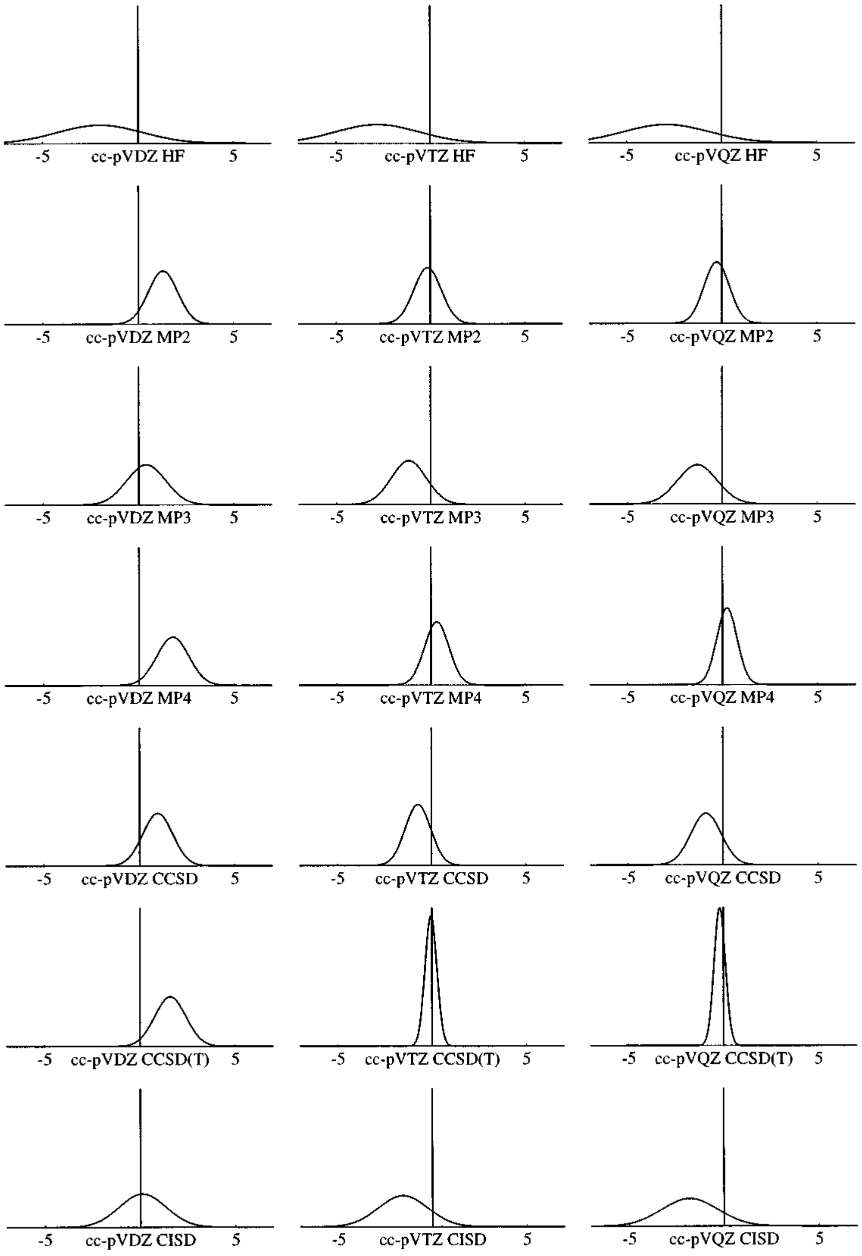
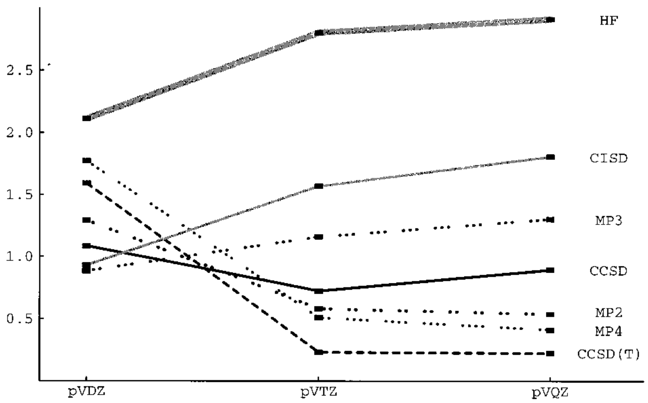
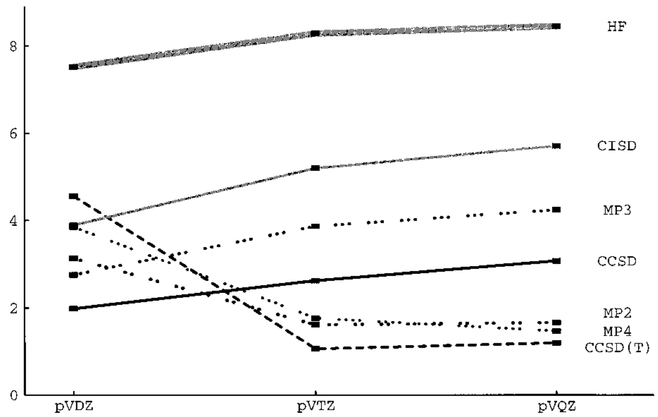


Figure 1.17: Normal distributions for the errors in calculated bond distances. Reproduced from: Helgaker *et al.*, J. Chem. Phys. **106**, 6430 (1997).



	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF	2.11	2.80	2.91
MP2	1.29	0.58	0.54
MP3	0.88	1.16	1.30
MP4	1.77	0.51	0.41
CCSD	1.09	0.72	0.89
CCSD(T)	1.59	0.23	0.22
CISD	0.93	1.57	1.80

Figure 1.18: Mean absolute errors $\bar{\Delta}_{abs}$ relative to experiment in calculated bond distances, pm (10^{-12}m=0.01 Å). Reproduced from: Helgaker *et al.*, J. Chem. Phys. **106**, 6430 (1997).



	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF	7.52	8.29	8.45
MP2	3.16	1.62	1.67
MP3	2.75	3.87	4.24
MP4	3.84	1.77	1.48
CCSD	1.98	2.62	3.07
CCSD(T)	4.55	1.07	1.20
CISD	3.89	5.19	5.72

Figure 1.19: Maximum errors Δ_{max} in calculated bond distances, pm (10^{-12}m=0.01 Å). Reproduced from: Helgaker *et al.*, J. Chem. Phys. **106**, 6430 (1997).

Chapter 2

Slater Rules and many electron wave-functions

Here we consider some general properties of many-electron wave-functions and how to work with them (formalisms).

A valid many-electron function must be normalized:

$$< \Psi|\Psi >= \int_{-\infty}^{+\infty} \Psi^*(\boldsymbol{x})\Psi(\boldsymbol{x})d\boldsymbol{x} \tag{2.1}$$

and must be antisymmetric to interchange of any 2 electrons — the Pauli principle.

Simplest n-electron antisymmetric functions: determinant composed of n different 1-electron functions:

$$|\Psi(\boldsymbol{r}) >= \frac{1}{\sqrt{n!}} det\{\phi_1\phi_2 \dots \phi_n\} =$$
$$\frac{1}{\sqrt{n!}} \begin{pmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_n(2) \\ \dots \\ \phi_1(n) & \phi_2(n) & \dots & \phi_n(n) \end{pmatrix} \tag{2.2}$$

Note that electron labels include not only the coordinates of the electrons, $\boldsymbol{r}_i$, but also spin, $\boldsymbol{s}_i$. Thus we call the 1 electron functions “spin-orbitals”

2.1 Orbitals and many-electron wave-functions

2.1.1 Orbitals: one-electron wave-functions

One-electron wave-function is called orbital, more precisely, spin-orbital, since it depends on spacial and spin coordinates of the electron: $\psi(\boldsymbol{x}) = \phi(\boldsymbol{r})s(\sigma)$, where $\boldsymbol{r}$ — spacial coordinate of the electron, and σ — spin coordinate of the electron.

Spacial part of the spin-orbital, $\phi(\boldsymbol{r})$, is called spacial orbital. One-electron spin-functions $s(\sigma)$ are simple: $\alpha(\sigma)$ corresponds to the spin up, $\beta(\sigma)$ — to the spin down. Spin-functions are orthonormal: $< \alpha|\alpha >=< \beta|\beta >= 1$, $< \alpha|\beta >= 0$.

From the set of N spacial orbitals, $\{\phi_i(\boldsymbol{r})\}_i^N$, we can generate 2N set of spin-orbitals: $\{\phi_i(\boldsymbol{r})\alpha, \phi_i(\boldsymbol{r})\beta\}_i^N$, α and β subsets are mutually orthonormal.

2.1.2 Two-electron wave-functions

Let us compose two-electron wave-function from one-electron wave-functions: $|\Psi(\boldsymbol{r},\sigma)>=\phi_1(1)\phi_2(2)$.

Bosons and fermions

Bosons: symmetric Ψ_{12}:

$$|\Psi(\boldsymbol{r},\sigma)>=\hat{P}_s\phi_1(1)\phi_2(2)=\frac{1}{\sqrt{2}}(\phi_1(1)\phi_2(2)+\phi_1(2)\phi_2(1)) \tag{2.3}$$

Fermions: anti-symmetric Ψ_{12}:

$$|\Psi(\boldsymbol{r},\sigma)>=\hat{P}_{as}\phi_1(1)\phi_2(2)=\frac{1}{\sqrt{2}}(\phi_1(1)\phi_2(2)-\phi_1(2)\phi_2(1)) \tag{2.4}$$

Can two particles occupy the same spin-orbital? Let us look at $|\Psi(\boldsymbol{r})>$ when $\phi_1=\phi_2\equiv\phi$:
Bosons: $|\Psi(\boldsymbol{r},\sigma)>=\phi(1)\phi(2)$ — OK
Fermions: $|\Psi(\boldsymbol{r},\sigma)>\equiv 0$ — NOT

Conclusion: there can be equivalent bosons in the system, but not equivalent fermions. There cannot be two electrons with the equivalent spacial and spin wave-functions (Pauli exclusion principle).

2.2 Slater determinants

Note that two-electron wave-function (2.4) can be written as the following determinant

$$|\Psi(\boldsymbol{r},\sigma)>=\frac{1}{\sqrt{2}}\begin{pmatrix}\phi_1(1) & \phi_2(1)\\ \phi_1(2) & \phi_2(2)\end{pmatrix}=\frac{1}{\sqrt{2}}(\phi_1(1)\phi_2(2)-\phi_1(2)\phi_2(1)) \tag{2.5}$$

This result can be readily generalized to the case of n-electron wave-functions:

$$\begin{aligned}|\Psi(\boldsymbol{r})>=\frac{1}{\sqrt{n!}}det\{\phi_1\phi_2\dots\phi_n\}=&\\ |\phi_1\phi_2\dots\phi_n>=&\\ \frac{1}{\sqrt{n!}}\begin{pmatrix}\phi_1(1) & \phi_2(1) & \dots & \phi_n(1)\\ \phi_1(2) & \phi_2(2) & \dots & \phi_n(2)\\ \dots & & & \\ \phi_1(n) & \phi_2(n) & \dots & \phi_n(n)\end{pmatrix}&\end{aligned} \tag{2.6}$$

Such form of antisymmetric wave-function is called Slater determinant (SD). Note that electron labels include not only the coordinates of the electrons, $\boldsymbol{r}_i$, but also spin, $\boldsymbol{s}_i$. Thus we call the 1-electron functions “spin-orbitals”

Note:

- interchange of two rows of the SD → interchange of two electrons → change sign of the SD.
- if there are two equivalent columns/rows → SD=0
- Scalar product of two SD composed from orthonormal orbitals: $< \Phi_i|\Phi_j >= 0$ if Φ_i,Φ_j differ by at least one orbital; if orbital set is the same $< \Phi_i|\Phi_j >= \pm 1$

At home: demonstrate the last point using 2-electron wave-function.

When we compare two SD, we reorder orbitals to be of the maximum coincidence, and only then calculate differences.

Example: Compare $|ijkl>$ and $|alji>$
1. Reorder second determinant: $|alji>$=-$|alij>$=...=-$|ijal>$.
2. Compare: determinants are different by ONE orbital.

2.2.1 Matrix elements of electronic Hamiltonian

Electronic Hamiltonian (n electrons, N nuclei):

$$\begin{aligned} H_{el} = V_{nn} - \sum_i^n \frac{\boldsymbol{p}_i^2}{2} \\ -\sum_i^n \sum_A^N \frac{Z_A}{|\boldsymbol{r}_i - \boldsymbol{R}_A|} + \sum_{i>j}^n \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \\ V_{nn} + \sum_i \hat{h}(i) + \frac{1}{2}\sum_{ij}^n \hat{v}(i,j), \end{aligned} \tag{2.7}$$

where V_{nn} is nuclear repulsion energy (constant), $\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{|R_A - r_i|}$ is a one-electron operator (kinetic energy of electrons and Coulomb attraction to nuclei), and $\hat{v}(i,j) = \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$ is a two-electron operator (Coulomb electron-electron repulsion).

Total electronic Hamiltonian can be written as follows:

$$H = \hat{O}_1 + \hat{O}_2 + V_{nn} \tag{2.8}$$

$$\hat{O}_1 = \sum_i^n \hat{h}(i) \tag{2.9}$$

$$\hat{O}_2 = \frac{1}{2}\sum_{ij}^n \hat{v}(i,j) \tag{2.10}$$

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A^N \frac{Z_A}{|R_A - r_i|} \tag{2.11}$$

$$\hat{v}(i,j) = \frac{1}{|r_i - r_j|}, \tag{2.12}$$

where $\hat{O}_1, \hat{O}_2$ represent one- and two-electron parts of the electronic Hamiltonian, respectively, and V_{nn} is a nuclear repulsion energy.

Notations for matrix elements

Matrix elements of one- and two- electron operators are called one- and two- electron integrals. We shall use so called physicist's notations and use spin-orbitals. (There are also chemist's notations, and, also, notations for integrals over spacial orbitals).

$$\begin{aligned} < i|h|j > &\equiv \\ < \phi_i(1)|h(1)|\phi_j(1) >_1 &= \\ \int d\boldsymbol{x}\phi_i^*(\boldsymbol{x})h(\boldsymbol{r})\phi_i(\boldsymbol{x}) & \end{aligned} \tag{2.13}$$

$$\begin{aligned} < ij|kl > &\equiv \\ < \phi_i(1)\phi_j(2)|v(r_{12})|\phi_k(1)\phi_l(2) >_{1,2} &= \\ \int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \phi_i^*(\boldsymbol{x}_1)\phi_j^*(\boldsymbol{x}_2)v(r_{12})\phi_k(\boldsymbol{x}_1)\phi_l(\boldsymbol{x}_2) & \\ < ij||kl > \equiv < ij|kl > - < ij|lk > & \end{aligned} \tag{2.14}$$

Permutational symmetry of integrals

Prove at home that:

$$< i|h|j > = < j|h|i >^* \tag{2.15}$$

$$\begin{aligned} < ij|kl > = < ji|lk > &= \\ < kl|ij >^* = < lk|ji >^* &= \\ < ij||kl > = < ji||lk > &= \\ < kl||ij >^* = < lk||ji >^* &= \\ - < ij||lk > = - < ji||kl > &= \\ - < lk||ij >^* = - < kl||ji >^* & \end{aligned} \tag{2.16}$$

2.2.2 Slater rules for matrix elements

Matrix elements between Slater determinants of n-electron system

$Case(\|K >, \|L >)$	$< K\|\hat{O}_1\|L >$	$< K\|\hat{O}_2\|L >$
$\|K >= \|\ldots mn\ldots >$ $\|L >= \|\ldots mn\ldots >$	$\sum_m^N < m\|h\|m >$	$\frac{1}{2}\sum_m^N\sum_n^N < mn\|\|mn >$
$\|K >= \|\ldots mn\ldots >$ $\|L >= \|\ldots pn\ldots >$	$< m\|h\|p >$	$\sum_n^N < mn\|\|pn >$
$\|K >= \|\ldots mn\ldots >$ $\|L >= \|\ldots pq\ldots >$	0	$< mn\|\|pq >$
$\|K >= \|\ldots mnl\ldots >$ $\|L >= \|\ldots pqr\ldots >$	0	0

Don't forget to reorder determinants to the maximum coincidence.

Slater Rules give all the necessary tools to work with Slater Determinants. However, it is possible to introduce a more convenient formalism, namely, Second Quantization operators.

2.2.3 Second Quantization formalism: a tool to derive electronic structure equations

What's for?

Second quantization allows us (i) to work with many-particle system with an arbitrary number of particles; and (ii) to transform (permutational) symmetry of the determinantal wave-function into algebraic equations.

1. With each spin-orbital ϕ_i associate a creation operator $\hat{a}_i^+$. Definition of $\hat{a}_i^+$: for any Slater determinant, $|k \dots l>$, operator $\hat{a}_i^+$ creates electron on $i-th$ orbital: $\hat{a}_i^+|k \dots l>=|ik \dots l>$.
   Consider two operators $\hat{a}_i^+$ and $\hat{a}_j^+$:
   $\hat{a}_i^+\hat{a}_j^+|k \dots l>=|ijk \dots l>$
   $\hat{a}_j^+\hat{a}_i^+|k \dots l>=|jik \dots l>=-|ijk \dots l>$

   Thus, anti-commutation relation:

   $$\{\hat{a}_i^+, \hat{a}_j^+\} \equiv \hat{a}_i^+\hat{a}_j^+ + \hat{a}_j^+\hat{a}_i^+ = 0 \tag{2.17}$$

   Note, that $\hat{a}_i^+\hat{a}_i^+ = 0$ (satisfy Pauli exclusion principle).

2. Annihilation operator $\hat{a}_i$ is defined as an adjoint of the creation operator:
   $\hat{a}_i = (\hat{a}_i^+)^+$
   What does annihilation operator $\hat{a}_i$ do? $\hat{a}_i$ destroys electron on the orbital i:
   $\hat{a}_i|ik \dots l>=|k \dots l>$
   $\hat{a}_i|ki \dots l>=-\hat{a}_i|ik \dots l>=-|k \dots l>$
   Why adjoint?
   Consider $|K>=|ij>=\hat{a}_i^+|j>$
   Take the adjoint of $|K>$: $((AB)^+ = B^+A^+)$
   $(|K>)^+ =<K| =<j|(\hat{a}_i^+)^+$
   We must satisfy $<K|K>=1$:
   $<K|K>=<j|(\hat{a}_i^+)^+\hat{a}_i^+|j>=<j|(\hat{a}_i^+)^+|ij>$
   In order to satisfy $<K|K>=1$ operator $(\hat{a}_i^+)^+$ must delete electron on orbital i.

   Anti-commutation relation:

   $$\{\hat{a}_i, \hat{a}_j\} \equiv \hat{a}_i\hat{a}_j + \hat{a}_j\hat{a}_i = 0 \tag{2.18}$$

   Note, that $\hat{a}_i\hat{a}_i = 0$ — cannot delete electron twice.

3. Anti-commutator of $\hat{a}_i^+\hat{a}_j$:

   $$\{\hat{a}_i^+, \hat{a}_j\} \equiv \hat{a}_i^+\hat{a}_j + \hat{a}_j\hat{a}_i^+ = \delta_{ij} \tag{2.19}$$

4. Vacuum state $|>$ — empty state, no electrons. $<|>=1$

Second Quantization: Summary

1. Vacuum state ≡ empty state $| >$, $< | >= 1$

2. Creation operator $\hat{a}_i^+$ ≡ creates electron on orbital i; $\hat{a}_i^+| >= |i >$, $\hat{a}_i^+\hat{a}_i^+ = 0$, $\hat{a}_i^+|i >= 0$,

3. Annihilation operator $\hat{a}_i$ ≡ destroys electron on orbital i; $\hat{a}_i|i >= | >$, $\hat{a}_i\hat{a}_i = 0$, $\hat{a}_i| >= 0$

4. Anti-commutation relations:

$$\begin{aligned}
(\hat{a}_i^+)^+ &= \hat{a}_i \\
\{\hat{a}_i^+, \hat{a}_j^+\} \equiv \hat{a}_i^+\hat{a}_j^+ + \hat{a}_j^+\hat{a}_i^+ &= 0 \\
\{\hat{a}_i, \hat{a}_j\} \equiv \hat{a}_i\hat{a}_j + \hat{a}_j\hat{a}_i &= 0 \\
\{\hat{a}_i^+, \hat{a}_j\} \equiv \hat{a}_i^+\hat{a}_j + \hat{a}_j\hat{a}_i^+ &= \delta_{ij}
\end{aligned} \tag{2.20}$$

5. Slater determinant, $\hat{O}_1$ and $\hat{O}_2$:

$$|ijk \dots l >= \hat{a}_i^+\hat{a}_j^+\hat{a}_k^+ \dots \hat{a}_l^+$$

$$\hat{O}_1 = \sum_{pq}^{M} < p|h|q > \hat{a}_p^+\hat{a}_q$$

$$\hat{O}_2 = \frac{1}{2}\sum_{pqrs}^{M} < pq|rs > \hat{a}_p^+\hat{a}_q^+\hat{a}_s\hat{a}_r = \frac{1}{4}\sum_{pqrs} < pq||rs > \hat{a}_p^+\hat{a}_q^+\hat{a}_s\hat{a}_r, \tag{2.21}$$

where M is number of spin-orbitals (sums run over the set of spin-orbitals).

Meaning of $\hat{O}_1$: it can change state of one electron. Thus, deletes one electron in state q, then creates electron in state p. Two-electron operator: change state of two electrons.

Now we can derive Slater rules, calculate overlap and matrix elements between different Slater determinants.

Second Quantization: Examples

How do we employ creation/annihilation operators? Let us consider several examples. From now on, I shall use following (simplified) notations:

$$p \equiv \hat{a}_p \tag{2.22}$$

$$p^+ \equiv \hat{a}_p^+ \tag{2.23}$$

$$|i >\equiv |\phi_i(x) > \tag{2.24}$$

$$\tag{2.25}$$

Ani-commutation properties $\{i, j\} = 0, \{i^+, j^+\} = 0$ means that if we are given a sequence of creation (or annihilation) operators, we can reorder them as we please (a change of sign must be accounted for):

$$ijkl = -jikl = jilk \tag{2.26}$$

$$i^+j^+k^+l^+ = -j^+i^+k^+l^+ = j^+i^+l^+k^+ \tag{2.27}$$

$$\tag{2.28}$$

However, if we have a string of creation *and* annihilation operators, interchange is not that simple:

$$ij^+ = \delta_{ij} - j^+i \tag{2.29}$$

How do we simplify expressions? We remember that certain combinations equal zero: $i| >= 0$, or $< |i^+ = 0$.

What about determinants? Consider $|\Phi >= a_1^+ \dots a_n^+| >$. $p^+|\Phi >$ equals to zero if orbital p is occupied in Φ (if operator p^+ can be found in the string). Why? We can reorder creation operators as we want, then combination p^+p^+ will give zero. $p|\Phi >$ is zero is p *is not* occupied in $\Phi >$, and non-zero otherwise. Similarly, we can work out rules for bra-determinants.

1. How to calculate overlap $< \Phi|\Phi >$?

$$< \Phi|\Phi >=< |a_n \dots a_1 a_1^+ \dots a_n^+| > \tag{2.30}$$

   Consider pair $a_1 a_1^+ = 1 - a_1^+ a_1$. Second term will give zero, since we can interchange a_1 with all $a_i^+, i \neq 1$ until we have $\dots a_1| >$, which is zero. Performing the same procedure of with all the rest of pairs of operators we finally have $< | >= 1$.

2. Let us now consider some *reference* determinant:

$$|\Phi_0 >= a_1^+ \dots a_n^+| > \tag{2.31}$$

   I will call the orbitals present in $|\Phi_0 >$ *occupied*, and I'll use indexes $i, j, k, l, \dots$ for them. I will call all the rest of orbitals *virtual* orbitals and will use $a, b, c, d \dots$ for them. When I need to refer to the orbitals which can be either occupied or virtual, I will use indexes $p, q, r, s, \dots$.

   Now consider determinants generated from $|\Phi_0 >$ by substituting one (occupied) orbital by a virtual orbital. $|\Phi_i^a >$ stands for the determinant where all orbitals are the same as in $\Phi_0 >$ except for the orbital i which is replaced by orbital a. How do we describe this determinant by second quantization?

$$|\Phi_i^a >= a^+i|\Phi_0 > \tag{2.32}$$

   Similarly, doubly substituted determinants denoted:

$$|\Phi_{ij}^{ab} >= a^+ib^+j|\Phi_0 >= -a^+b^+ij|\Phi_0 >= a^+b^+ji|\Phi_0 > \dots \tag{2.33}$$

3. Excitation operators $\hat{C}_n$: generate *all possible* n-tuple excitations from $|\Phi_0>$ with arbitrary amplitudes:

$$\hat{C}_1 = \sum_{ia} c_i^a a^+ i \tag{2.34}$$

$$\hat{C}_2 = \sum_{i<j,a<b} c_{ij}^{ab} a^+ b^+ ji = \frac{1}{4} \sum_{ijab} c_{ij}^{ab} a^+ b^+ ji \tag{2.35}$$

$$\ldots \tag{2.36}$$

Factor $\frac{1}{4}$ accounts for the fact that the sum over i, j ad a, b is unrestricted and includes redundant cases, i.e., both i, j and j, i. That could be avoided by restricting sum for $i < j$ and $a < b$. That's how they work:

$$\hat{C}_1 \Phi_0 = \sum_{ia} c_i^a \Phi_i^a \tag{2.37}$$

$$\hat{C}_2 \Phi_0 = \frac{1}{4} \sum_{ijab} c_{ij}^{ab} \Phi_{ij}^{ab} \tag{2.38}$$

4. Prove that two excitation operators commute.

5. Consider two determinants: $|\Phi >= a_1^+ \ldots a_i^+ \ldots a_n^+| >$ and a single-substituted determinant $\Phi_i^a = a_1^+ \ldots a_a^+ \ldots a_n^+| >$, in which ith orbital was replaced by ath orbital. In a second quantization form, $\Phi_i^a = a^+ i|\Phi >$ (see above discussion). Overlap $< \Phi|\Phi_i^a >=< \Phi|a^+ i|\Phi >= 0$ if a is not equal to i. $a^+ i = \delta_{ai} - ia^+$, where second term is zero.

6. Consider operator $\hat{N} = \sum_{p=0}^{M} p^+ p$, M is number of spin-orbitals. For a general n-electron normalized wave-function $\Psi = \sum_L C_L \Phi_L$, show that $< \Psi|\hat{N}|\Psi >= n$, where n is a number of electrons.

   For a determinant Φ_L:
   $p^+ p \Phi_L$ is zero if $p \notin \Phi_L$ and Φ_L otherwise. Thus, $\sum_{p=0}^{M} p^+ p \Phi_L = n\Phi_L$, since n defines how many spin-orbitals are in Φ_L. Thus, $< \Psi|\hat{N}| \sum_L C_L \Phi_L >=< \Psi| \sum_L C_L n \Phi_L >= n < \Psi| \sum_L C_L \Phi_L >= n < \Psi|\Psi >= n$.

   Operator $\hat{N} = \sum_{p=0}^{M} p^+ p$ is called a number operator.

7. Consider matrix elements of one-electron part of the Hamiltonian:

$$< \Phi_0|\hat{O}_1|\Phi_0 >= \sum_{pq}^{M} < p|h|q >< \Phi_0|p^+ q|\Phi_0 >= \sum_{p \in \Phi_0} < p|h|p >= \sum_{i} < i|h|i > \tag{2.39}$$

8. Consider matrix elements of $\hat{O}_1$ between the reference and single-substituted determinants:

$$< \Phi_i^a|\hat{O}_1|\Phi_0 >= \sum_{pq} < \Phi_0|i^+ a p^+ q|\Phi_0 >< p|h|q >=$$

$$\begin{aligned}
\sum_{pq} < \Phi_0 | i^+ (\delta_{ap} - p^+ a) q | \Phi_0 >< p | h | q > = \\
\sum_{pq} < \Phi_0 | \delta_{ap} (\delta_{iq} - q i^+) - i^+ p^+ (\delta_{aq} - q a) | \Phi_0 >< p | h | q > = \\
< a | h | i >
\end{aligned} \tag{2.40}$$

Term $...qi^+$ is zero because i is already occupied in Φ_0. For the same reason, $...i^+p^+...$ term is zero (can interchange two creation operators). Similarly, $...qa...$ is zero because a is not present in Φ_0.

Chapter 3

Hartree-Fock model: one-electron approximation

Now, when we have our tools, i.e., second quantization or Slater Rules, we can start to discuss approximations to electronic Schrödinger equation. Recall how we can find an exact solution: start from a complete 1-electron basis set, generate a complete n-electron basis set (Slater determinants), expand the wave-function over the n-electron basis set, find expansion coefficients from variational principle. This procedure is unrealistic. Thus, we introduce approximations to (i) 1-electron basis; and (ii) n-electron basis.

We start from considering the simplest and crudest approximation (ii) — when wave-function is represented by a single Slater Determinant. We first consider what is a physical meaning of such approximation and then we will discuss how to do it, i.e., how to find a Slater Determinant which is the best possible approximation to the exact wave-function.

References:.[12,13] To do: find original Roothan paper.

3.1 Non-interacting electron gas

In your homework, you have seen that for the separable Hamiltonian $H = \sum_i^n h(i)$ wave-function $\Phi(x_1, \ldots, x_n) = \phi_i(x_1)\phi_j(x_2)\ldots\phi_k(x_n)$, where one-particle functions are eigenstates of one-particle Hamiltonian:

$$h(i)\phi_k(x_i) = \epsilon_k \phi_k(x_i) \tag{3.1}$$

with an energy $E = \epsilon_i + \epsilon_j + \ldots + \epsilon_k$.

Now let us consider system of n non-interacting electrons, i.e., $\hat{O}_2$=0:

$$H = \hat{O}_1 = \sum_i^n h(i) \tag{3.2}$$

Using second quantization, we shall see that any Slater determinant composed of n spin orbitals which are eigenstates of h is an eigenstate of H.

First, let us analyze $\hat{O}_1$:

$$\hat{O}_1 = \sum_{pq}^{M} < p|h|q > p^+q = \sum_{p}^{M} < p|h|p > p^+p = \sum_{p}^{M} \epsilon_p p^+p \tag{3.3}$$

since orbitals p are eigenstates of h. Consider now $H|\Phi >= \sum_p^M < p|h|p > p^+p|\Phi >= \sum_{p\in\Phi} < p|h|p > p^+p|\Phi >= \sum_{p\in\Phi} < p|h|p > (1 - pp^+|\Phi >= \sum_{p\in\Phi} < p|h|p > |\Phi >= \sum_{p\in\Phi} \epsilon_p|\Phi >$

Ground state for the system of non-interacting electrons is given by SD in which n lowest spin-orbitals are populated, $\Phi_{gs} = \Phi_0$. Excited states are given by excited (substituted) SD: $\Phi_i^a, \Phi_{ij}^{ab}, \ldots$. Excitation energies are given by one-electron energies, e.g., $E(\Phi_0 - > \Phi_i^a) = \epsilon_a - \epsilon_i$. This is because electrons do not interact and therefore excitation of one electron does not change states of other electrons.

3.2 Interacting electrons: mean-field model

If electrons interact very weakly, we can expect that a single SD will be a reasonable approximation to the wave-function. However, we want to account (somehow) for electron interaction. Let us consider one-electron approximation, but when one-electron operators h for each electron include mean-field of all other electrons. This is a simplest electronic structure model, and it is called Hartree-Fock (self-consistent field) approximation: each electron moves in the mean-field of other electrons.

What other mean-field models do we know? Adiabatic approximation is a mean-field model: nuclei move in the mean-field of electrons. Recall:

$$(T_N + U(R))\xi = E\xi \tag{3.4}$$

$$U(R) =< \Phi_{el}|H_{el}|\Phi_{el} >_r \tag{3.5}$$

Can we justify mean-field model? In case of adiabatic approximation different velocities of electronic and nuclear motion provide such justification. In case of electrons this is not applicable — all electrons move with a same speed. Moreover, pair Coulomb interactions $\frac{1}{r_{ij}}$ are strong interactions, and electron can "see" the difference in a local arrangement of other electrons. So why such an approximation may work? Coulomb interactions are long range interactions. We can hope that long range effects summed over all electrons are strong enough to beat local pair (correlation) effects. Also, one electron part of the Hamiltonian is quite large — at least Coulomb interaction with a nuclei has same order of magnitude.

Aside: Would it work for a system of bosons? He cluster? Are coordinates important? Normal modes vs Cartesian (vibrational problem is separable in normal coordinates and is not separable in Cartesian). Why?

So, what is one-particle approximation? It assumes separability of the wave-function in a sense that

$$\begin{aligned} \Phi(1, \ldots, n) = \hat{A}s\left(\phi_1(1) \ldots \phi_n(n)\right) = |\phi_1(1) \ldots \phi_n(n) > \\ E_{tot} = \epsilon_1 + \ldots + \epsilon_n \\ h_{eff}\phi_i = \epsilon_i\phi_i \end{aligned} \tag{3.6}$$

What would one-electron approximations for electrons look like? What is an h_{eff}? Electronic Hamiltonian:

$$H_{el} = V_{nn} + \sum_i \hat{h}(i) + \frac{1}{2}\sum_{ij} \hat{v}(i,j), \tag{3.7}$$

One electron part $\hat{h}(i)$ is given by a kinetic energy of electrons and electrostatic interactions with nuclei. Two-electron part $\hat{v}(i,j)$ is a Coulomb interaction of electrons. Recall: Coulomb field by point charge q:

$$\phi(r) = \frac{q}{r} \tag{3.8}$$

Coulomb field by charge distribution $\rho(x)$:

$$\phi(r) = \int dx \frac{\rho(x)}{|r-x|} \tag{3.9}$$

Coulomb interaction of point charge q' with a field:

$$E = \phi(r)q' = \frac{q'q}{r} = q' \int dx \frac{\rho(x)}{|r-x|} \tag{3.10}$$

Coulomb interaction of charge distribution $\rho'(r)$ with a field:

$$E = \int dr \phi(r)\rho'(r) = \int dr \rho'(r)\frac{q}{r} = \int dr \rho'(r) \int dx \frac{\rho(x)}{|r-x|} \tag{3.11}$$

Consider Coulomb operator:

$$\hat{J}_\rho(1) = \int \frac{\rho(2)}{|r_1 - r_2|} d2, \tag{3.12}$$

where $\rho(1) = \int \Psi(1,2,\dots n)^* \Psi(1,2,\dots n)\ d2 \dots dn$ is an electronic density of all the electrons (probability to find an electron at the volume $d1 = dx_1 d\sigma_1$ at the $1 = (r_1, \sigma_1)$).

Interaction of one electron on orbital ϕ with average Coulomb potential is given by $\hat{J}_\rho(x)\phi(x)$. We have, though, to exclude one electron away (create a hole). Let us introduce exchange operator $\hat{K}(x)$ that acts as follows: when applied to ϕ_i ($\hat{K}(1)\phi_i(1)$) it "deletes" contribution from $\phi_i(1)$ in Coulomb operator. It is said that the exchange operator takes care of the self-interaction error (the interaction of an electron with itself).

Resulting form of effective separable (one-electron) Hamiltonian:

$$\hat{h}_{eff}(x) = \hat{h}(x) + \hat{J}(x) - \hat{K}(x) \tag{3.13}$$

3.3 Derivation of HF equations

3.3.1 Variational principle

If we are given an ansatz (a functional form) for the wave-function, how do we find a best function in this class? For example, consider a one electron function $\Psi(r;\alpha) = e^{-\alpha r}$ that depends on a parameter α. The VP tells us that the "best" value of α will minimize the expectation value $E(\alpha) =< \Psi(\alpha)|H|\Psi(\alpha) >$. Thus, the recipe is: (i) to obtain an analytic expression for the function E(α); (ii) take derivative, $\frac{\partial E}{\partial \alpha}$; (iii) solve for $\frac{\partial E}{\partial \alpha} = 0$.

When we consider more complex parameterization (e.g., we can vary functions themselves, and not just numeric coefficients), this can be generalized by using the concept of functional variation. Thus, the general form of the Rayleigh-Schrödinger VP is:

$$\delta \left(E = \frac{< \Phi|H|\Phi >}{< \Phi|\Phi >} \right) = 0 \tag{3.14}$$

What does it mean? We can see that for the exact wave-function, this is equivalent to the Schrödinger equation. What else?

The rules for taking a variation are the same as for taking a derivative. By using $\left(\frac{u}{v}\right)' = \frac{(u'v-uv')}{v^2}$ and $E = \frac{<\Phi|H|\Phi>}{<\Phi|\Phi>}$ we obtain:

$$\frac{< \delta\Phi|H-E|\Phi >}{< \Phi|\Phi >} + \frac{< \Phi|H-E|\delta\Phi >}{< \Phi|\Phi >} = 0 \tag{3.15}$$

For real-valued normalized wave-function this reduces to:

$$< \delta\Phi|H-E|\Phi >= 0 \quad or \quad < \delta\Phi|H|\Phi >= 0 \tag{3.16}$$

What does that mean? Consider 3D space, $\{x, y, z\}$ and some operator $\hat{H}$ operating on 3D vectors, e.g., $\hat{H}p = s$ (p, s are 3D vectors). This is shown in Fig. 3.1. Eigenproblem $\hat{H}r = \epsilon r$ means that when $\hat{H}$ operates on vector r the result, i.e. vector $\hat{H}r$, is *parallel* to vector r. Thus:

$$\hat{H}r = \epsilon r \quad <-> \quad (\hat{H}r)||r \quad <-> \quad (s, \hat{H}r) = 0 \quad <-> \quad (\delta r, \hat{H}r) = 0 \tag{3.17}$$

where s is any vector orthogonal to r. The last form uses the fact that a small variation is orthogonal to a vector.

Now consider 2D approximation (vector q from XY plane) of the vector r. How we can rewrite the original 3D problem for 2D vector? First, note that we cannot satisfy $\hat{H}q = \epsilon q$, since vector $\hat{H}q$ has Z-component, and vector q does not. However, we can minimize a norm of the vector $(\hat{H}q - \epsilon q)$. How to do that? Make (XY) component of the vector $\hat{H}q$ parallel to q. Thus, $(\delta q, \hat{H}q) = 0$, where δq is any *allowed* variation of q, i.e., it belongs to XY plane as well. This is explained in Fig. 3.2

This picture can be readily generalized to the case of non-linear spaces. Consider 2D nonlinear manifold, e.g., a surface of sphere in 3D space (let us simply bend our XOY plane). If we restrict our approximate function Φ to this manifold, than the

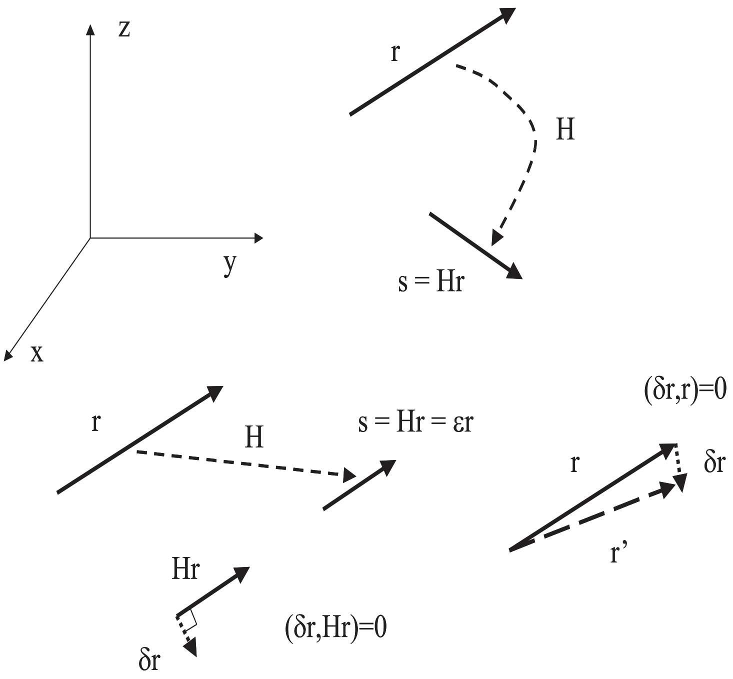


Figure 3.1: Consider 3D space and the operator $\hat{H}$ which operates on 3D vectors. For a vector r which is an eigenvector of operator H, i.e., $\hat{H}r = \epsilon r$, the vector $\hat{H}r$ is parallel to the vector r. Thus, it is orthogonal to any vector orthogonal to r. Therefore, it is also orthogonal to any small variation of vector r (since small variations are orthogonal to a varied vector). Thus, eigenproblem $\hat{H}r = \epsilon r$ is equivalent to the following condition: $(\delta r, \hat{H}r) = 0$.

$\hat{H}\Phi$ does not necessarily belongs to the manifold of trial functions — it will have tangential and orthogonal components. To minimize a difference $\hat{H}\Phi - \epsilon\Phi$ by varying Φ within the manifold means to zero out a tangential component of this vector. This, $< \delta\Phi|H\Phi >= 0$, where $\delta\Phi$ is an allowed variation of Φ. Allowed variations leave Φ within the manifold, and thus are tangential to the manifold.

So, we shall approximate electronic wave-function by a single Slater determinant and vary orbitals such that the energy is minimal preserving ortho-normality of orbitals:

$$\begin{aligned}
\{\phi_i\}_{i=1}^n, \quad < \phi_i|\phi_j >= \delta_{ij} \\
|\Psi_{HF} >= |\Phi_0 >= |1 \ldots n >= a_1^+ \ldots a_n^+ \\
< \Phi_0| =< n \ldots 1| = a_n \ldots a_1 \\
\mathrm{F}IND \quad min_\phi(E(\{\phi_i\}_1^n) =< \Phi_0|H|\Phi_0 >) \\
\mathrm{H}OLD \quad < \Phi_0|\Phi_0 >= 1
\end{aligned} \tag{3.18}$$

3.3.2 Expression for Hartree-Fock energy

$$E(\{\phi_i\}_1^n) =< \Phi_0|H|\Phi_0 >=< \Phi_0|\hat{O}_1|\Phi_0 > + < \Phi_0|\hat{O}_2|\Phi_0 > \tag{3.19}$$

One-electron terms:

$$< \Phi_0|\hat{O}_1|\Phi_0 >= \sum_{pq} < \Phi_0|a_p^+ a_q|\Phi_0 >< p|h|q > \tag{3.20}$$

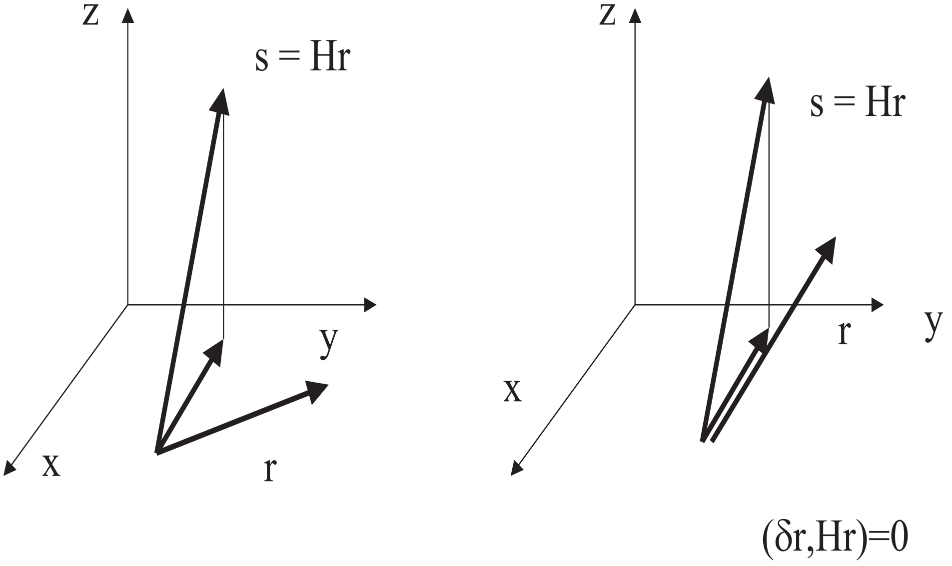


Figure 3.2: If vector r is restricted to a 2D subspace, we cannot exactly satisfy the eigenproblem $Hr = \epsilon r$, since the result Hr will, in general, have the component orthogonal to our 2D plane, i.e., Z component, whereas vector r is not allowed to have it. However, we still can choose r such that the vector $s = Hr$ is as parallel to r as our restriction allows. That means that we can make the 2D projection of vector s parallel to vector r. That, in turn, means, that the best approximation to 3D vector by 2D vector r is achieved when Hr is orthogonal to any allowed, i.e., that from 2D plane, variation of r. The approximate solution of the eigenproblem $\hat{H}r = \epsilon r$ is thus defined by the condition: $(\delta r, \hat{H}r) = 0$ (where r is approximate vector of reduced dimensionality, or restricted to a certain manifold, and δr is any allowed variation).

How do we derive one-electron contributions to energy?

1. Note that $a_q|\Phi_0>$ is non-zero only if $q \in \{1 \dots n\}$ — sum over q reduces to the sum over occupied orbitals only;

2. Similarly, $p \in \{1 \dots n\}$ — sum over p reduces to the sum over occupied orbitals only;

3. Interchange a_p^+ and a_q: $a_p^+ a_q = \delta_{pq} - a_q a_p^+$, here second term gives zero since $p, q \in \Phi_0$.

$$< \Phi_0|\hat{O}_1|\Phi_0 >= \sum_{i=1}^{N} < i|h|i > \tag{3.21}$$

Two-electron terms:

$$< \Phi_0|\hat{O}_2|\Phi_0 >= \frac{1}{2}\sum_{pqrs} < \Phi_0|a_p^+ a_q^+ a_s a_r|\Phi_0 >< pq|rs >= \frac{1}{2}\sum_{ij}^{N} < ij||ij > \tag{3.22}$$

Here we use indexes i, j instead of indexes p, q to emphasize that the indexes belongs to the subspace of orbitals occupied in Φ_0, i.e., $i, j \in \Phi_0$.

Hartree-Fock energy is:

$$E_{HF} =< \Phi_0|H|\Phi_0 >= \sum_{i=1}^{N} < i|h|i > + \frac{1}{2}\sum_{ij}^{N} < ij||ij > \tag{3.23}$$

We can treat HF energy as a sum of expectation values of one- and two-electron operators. Let us analyze these operators.

One electron contributions arise from matrix elements of one-electron part of the Hamiltonian, $< i|h|i >$. One electron operator h is simple: when applied to an electron on the orbital $|\phi_i >$ it involves differentiating the orbital (kinetic energy) and multiplying it by a number (potential energy of the interaction with nuclei).

Consider two electron integrals:

$$< ij|ij >= \int d1d2\ \phi_i(1)^*\phi_j(2)^*\frac{1}{r_{12}}\phi_i(1)\phi_j(2) =$$
$$\int d1\ \phi_i(1)^* \left(\int d2\ \frac{\phi_j(2)^*\phi_j(2)}{r_{12}} \right) \phi_i(1) =< \phi_i(1)|\hat{J}_j|\phi_i(1) > \tag{3.24}$$

where we defined a Coulomb operator $\hat{J}_j$ (effective one-electron operator) as:

$$\hat{J}_j\phi(1) = \int \phi_j^*(2) r_{12}^{-1} \phi_j(2) d2 \cdot \phi(1) \tag{3.25}$$

Note that the Coulomb operator $\hat{J}_j$ is a *local operator*. It describes a Coulomb potential created by electron on the orbital j. The total Coulomb operator is:

$$\hat{J}_\rho = \int \frac{\rho(2)}{|r_1 - r_2|} d2 = \int d2 \sum_j \phi_j^*(2) r_{12}^{-1} \phi_j^*(2) = \sum_j \hat{J}_j \tag{3.26}$$

Similarly,

$$< ij|ji >= \int d1d2\ \phi_i(1)^*\phi_j(2)^*\frac{1}{r_{12}}\phi_j(1)\phi_i(2) =$$
$$\int d1\ \phi_i(1)^* \left(\int d2\ \frac{\phi_j(2)^*\phi_i(2)}{r_{12}} \right) \phi_j(1) =< \phi_i(1)|\hat{K}_j|\phi_i(1) >, \tag{3.27}$$

with an *non-local* exchange operator:

$$\hat{K}_j\phi(1) = \int \phi_j^*(2) r_{12}^{-1} \phi(2) d2 \cdot \phi_j(1) \tag{3.28}$$

Why exchange? There is no classical analog. If we compare $\hat{J}_j\phi(x)$ and $\hat{K}_j\phi(x)$ we see that $\hat{K}_j$ interchange orbitals ϕ_j and ϕ_i.

Thus, Hartree-Fock energy is:

$$E_{HF} = \sum_i < i|h|i > + \frac{1}{2}\sum_{ij} < i|\hat{J}_j - \hat{K}_j|i > \tag{3.29}$$

I also define a Fock operator, an effective one-electron operator, as:

$$\hat{F}(1) = h(1) + \sum_j \left[\hat{J}_j(1) - \hat{K}_j(1)\right] \tag{3.30}$$

Fock operator includes one-electron terms (kinetic energy of electron and interaction with nuclei), Coulomb interaction of an electron with the electron density of all electrons corrected by subtraction of self-interactions. It looks like one-electron operator, but it depends on the all others electrons as well. Thus, Fock operator is a non-linear operator.

3.3.3 Derivation of Hartree-Fock equations

$$E_{HF} =< \Phi_0|H|\Phi_0 >= \sum_{i=1}^{N} < i|h|i > + \frac{1}{2}\sum_{ij}^{N} < ij||ij > \tag{3.31}$$

Vary orbitals ($i \to i + \delta_i$), collect first order terms to get δE, then find condition when $\delta E = 0$. Don't forget to keep orbitals orthonormal, $< i|j >= \delta_{ij}$, which satisfy ortho-normality of the total wave-function (optimization with constraint).

Energy variation:

$$\begin{aligned}\delta E = \sum_i [< \delta i|h|i > + < i|h|\delta i >] + \\ \frac{1}{2}\sum_{ij}[< \delta ij||ij > + < i\delta j||ij > + \\ < ij||\delta ij > + < ij||i\delta j >]\end{aligned} \tag{3.32}$$

Using permutational symmetry of 1- and 2-electron integrals and renaming summation indexes:

$$\delta E = \sum_i < \delta i|h|i > + \sum_{ij} < \delta ij||ij > + (\delta E)^* \tag{3.33}$$

Ortho-normality: restriction on variations δi. We shall use Lagrange multipliers to impose ortho-normality of the orbitals ($< i|j >= \delta_{ij}$):

$$\delta E = 0 \ \ \& \ \ < i|j > -\delta_{ij} = 0 \tag{3.34}$$

$$\delta\left(E - \sum_{ij}\epsilon_{ij}(< i|j > -\delta_{ij})\right) = 0 \tag{3.35}$$

Note, that Lagrange multipliers compose a Hermitian matrix — since orbital overlap matrix $< \phi_i|\phi_j >$ is a Hermitian matrix as well. In order to satisfy N independent conditions, we need to use N Lagrange multipliers.

$$\begin{aligned}\left(\sum_i < \delta i|h|i > + \sum_{ij} < \delta ij||ij > - \sum_{ij}\epsilon_{ij} < \delta i|j >\right) + \\ \{complex \ \ conjugate\} = 0\end{aligned} \tag{3.36}$$

Have to satisfy for both parts → vary independently
Have to satisfy for ANY δi →
Result:

$$h|i> + \sum_j \left[\hat{J}_j|i> - \hat{K}_j|i>\right] = \sum_j \epsilon_{ij}|j>$$
$$\hat{F}|i> = \sum_j \epsilon_{ij}|j> \tag{3.37}$$

Canonical Hartree-Fock equations

Consider unitary transformation $U$of orbitals:

$$\tilde{\phi}_i(x) = \sum_k \phi_k(x) U_{ki} \tag{3.38}$$

Thus, transformed row:

$$\left(\tilde{\phi}_1(x) \ldots \tilde{\phi}_n(x)\right) = (\phi_1(x) \ldots \phi_n(x))\, U \tag{3.39}$$

Transformed determinant is therefore:

$$|\tilde{\Phi}| = |\Phi U| \tag{3.40}$$

Note that unitary transformation of occupied orbitals does not change Φ_0, since $det(AB) = detA * detB$, and the determinant of unitary matrix equals unity. Therefore, we can look for such transformation of orbitals so that matrix ϵ_{ij} becomes diagonal matrix:

$$F|i> = \epsilon_i|i> \tag{3.41}$$

This are canonical HF-equations.

Equivalent form of HF equations:

$$< a|F|i> = 0, \tag{3.42}$$

where i is an occupied orbital and a is any orbital orthogonal to the subspace of occupied orbitals, i.e., a virtual orbital.

What we have done? We transformed one many-particle equation into set of coupled one-particle equations.

3.4 Orbital energies ϵ_i and Koopmans theorem

HF-energy is:

$$E_{HF} = \sum_{i=1}^{N} < i|h|i> + \frac{1}{2}\sum_{ij}^{N} < ij||ij> = \sum_i \epsilon_i - \frac{1}{2}\sum_{ij} < ij||ij>, \tag{3.43}$$

where orbital energies ϵ_i are:

$$\epsilon_i =< i|h|i > + \sum_j^N < ij||ij > \tag{3.44}$$

Note that Hartree-Fock energy is *not* a sum of effective one-electron energies ϵ_i. Why? Formally, we have lost factor of $\frac{1}{2}$ when we differentiated two-electron part of the energy. But what is a physical meaning of this fact?

To understand why $E_{tot} \neq \epsilon_1 + \dots \epsilon_n$, where $\epsilon_i =< i|F|i >=< i|h|i > + < i|J|i > - < i|K|i >$, consider 2-electrons-on-2-orbitals i, j (ϵ_i and ϵ_j). $\epsilon_i =< i|F|i >=< i|h|i > + < i|J_j|i > - < i|K_j|i >$ includes interaction of the electron on orbital i with the electron on j. Similarly, ϵ_j includes interaction of the electron on j with an electron on a. Hence, $i - j$ interaction calculated twice.

Is there any physical meaning of orbital energies? Koopmans theorem says that orbital energy ϵ_i gives an ionization potential from the orbital i in a frozen core approximation:

$$IP =^{N-1} E_i -^N E_0 = -\epsilon_i \tag{3.45}$$

Frozen core approximation means that orbitals do not change when one electron is removed from the molecule. At home: prove the Koopmans theorem by calculating energy differences between systems of N and $N-1$ electrons.

3.5 Brillouin's theorem

Another important property of Hartree-Fock determinant Φ_0 is that matrix elements between HF determinant and any singly excited determinant are zero:

$$< \Phi_i^a|H|\Phi_0 >= 0 \tag{3.46}$$

Why? $< \Phi_i^a|H|\Phi_0 >=< a|F|i >= 0$

Another way to prove it is (1) to show that for real-valued function $< \delta\Phi|H|\Phi_0 >= 0$ from VP, and (2) to show that first variation of the determinant $\delta\Phi_0$ is given by a single excited determinants, i.e., $\delta\Phi_0 = \sum_{ia} c_i^a \Phi_i^a$. Prove at home.

Aside: If we consider the entire space of many-electron wave-functions $\{\Phi_0,\ \Phi_i^a,\ \Phi_{ij}^{ab}\}$, in which subspace HF wave-function is defined? In a subspace of reference and single excitations

3.6 Molecular Orbitals — Linear Combination of Atomic Orbitals (MOLCAO) approach

Eq. (3.41) is an operator equation, i.e., differential equation. As a next step, we are going to transform Eq. (3.41) to some set of linear equations. This will be done by representing eigenstates of the Fock operators, ϕ_i (molecular orbitals) by a linear combination of atomic orbitals (MOLCAO). There are several implementations of

MO-LCAO approach: (i) Hartree-Fock-Roothaan equations (RHF); (2) Pople-Nesbet equations (UHF); and (3) Restricted Open-Shell HF (ROHF).

Introduce AO basis: $\phi_i = \sum_\mu C_{\mu i}\xi_\mu$, $\mu = 1\dots M, i = 1\dots N$. The matrix C is called molecular orbital matrix. It defines molecular orbitals as a linear combination of atomic orbitals, $C_{\mu i}$ is a coefficient giving the contribution of AO μ to MO i. AO's $\{\xi\}$ are not orthonormal: $< \xi_\mu|\xi_\nu >= S_{\mu\nu} = S_{\mu\nu}$, S is thus an overlap matrix for atomic orbitals $\{\xi\}$. MO $\{\phi\}$ are orthonormal:

$$\begin{aligned} < \phi_i|\phi_j >= \delta_{ij} = \\ \sum_{\mu=1}^{M}\sum_{\nu=1}^{M} C_{\mu i} < \xi_\mu|\xi_\nu > C_{\nu j} = \\ \sum_{\mu=1}^{M}\sum_{\nu=1}^{M} C_{\mu i}S_{\mu\nu}C_{\nu j} = \left[C^+SC\right]_{ij} => \\ C^+SC = \hat{1} \end{aligned} \tag{3.47}$$

To obtain equations for coefficients C we apply a Linear Variational Principle (LVP). LVP answers the following question: what are best $C_{i\mu}$? Variationally they minimize E:

$$E = \frac{< \Phi|H|\Phi >}{< \Phi|\Phi >} \tag{3.48}$$

Resulting MO-LCAO equations are:

$$FC = SCE \tag{3.49}$$

$$C^+SC = 1 \tag{3.50}$$

where F is a matrix of Fock operator in AO basis:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma}^{M} < \mu\lambda||\nu\sigma > P_{\lambda\sigma} \tag{3.51}$$

where P is a density matrix:

$$P_{\lambda\sigma} = \sum_{i=1}^{N} C_{\lambda i}C_{\sigma i} \tag{3.52}$$

Let us analyze Eqns. (3.49,3.50):

$$FC = SCE \quad => \quad C^+FC = C^+SCE \quad => \quad C^+FC = E, \tag{3.53}$$

Which means that Fock matrix is diagonal in the basis of final MOs. Thus, Eqns. (3.49,3.50) are nothing but generalized matrix eigenproblem.

Why P from Eq. (3.52) is called density matrix? Electronic density, i.e., probability to find an electron at point x:

$$\rho(x_1) = \int \Psi(x_1, x_2, \dots, x_n)\Psi(x_1, x_2, \dots, x_n)dx_2 \dots dx_n \tag{3.54}$$

For $\Psi \equiv \Phi_0$ (a single Slater determinant):

$$\begin{gathered}\rho(x_1) = \int \Phi_0(x_1, x_2, \dots, x_n)\Phi_0(x_1, x_2, \dots, x_n)dx_2 \dots dx_n = \\ \int \hat{A}_s\left[\phi_1(x_1)\phi_2(x_2)\dots\phi_n(x_n)\right] \times \hat{A}_s\left[\phi_1(x_1)\phi_2(x_2)\dots\phi_n(x_n)\right] dx_2 \dots dx_n = \\ \sum_{i=1}^{N} \phi_i^2(x_1), \end{gathered} \tag{3.55}$$

where $\hat{A}_s$ is anti-symmetrizing operator. This is a very sensible result — for non-interacting electrons, the probability to find an electron is sum over one-electron probabilities (electrons are independent, and so are the probabilities!).

By substituting $\phi_i = \sum_\mu C_{\mu i}\xi_\mu$ into the above expression for density:

$$\begin{gathered}\rho(x) = \sum_{i=1}^{N} \phi_i^2(x) = \\ \sum_{i=1}^{N}\sum_{\mu=1}^{M}\sum_{\nu=1}^{M} C_{\mu i}\xi_\mu C_{\nu i}\xi_\nu = \sum_{\mu\nu} P_{\mu\nu}\xi_\mu\xi_\nu\end{gathered} \tag{3.56}$$

Matrix P thus tells us how to calculate electronic density once molecular orbital coefficients are known.

3.6.1 Linear Variational Principle

Here is a brief description of LVP.

$$\begin{gathered}|\psi> = \sum_k C_k|\xi_k> \\ E = \frac{<\Phi|H|\Phi>}{<\Phi|\Phi>} = \\ \frac{\sum_{kl} C_k C_l <\xi_k|H|\xi_l>}{\sum_{kl} <\xi_k|\xi_l> C_k C_l}\end{gathered} \tag{3.57}$$

Consider, when $\frac{\partial E}{\partial C_i} = 0$. Do this as an implicit derivative:

$$\begin{gathered}\frac{\partial E}{\partial C_i} = \frac{1}{(\sum_{kl} <\xi_k|\xi_l> C_k C_l)^2} \\ 2\sum_m C_k <\xi_m|H|\xi_i> \sum_{kl} <\xi_k|\xi_l> C_k C_l - \\ 2\sum_m <\xi_m|\xi_i> C_m \sum_{kl} C_k C_l <\xi_k|H|\xi_l>\end{gathered} \tag{3.58}$$

To satisfy $\frac{\partial E}{\partial C_i} = 0$, we need to zero numerator:

$$0 = 2\sum_m C_k <\xi_m|H|\xi_i> \sum_{kl} <\xi_k|\xi_l> C_k C_l -$$

$$\begin{aligned} 2\sum_m < \xi_m|\xi_i > C_m \sum_{kl} C_k C_l < \xi_k|H|\xi_l > \\ \sum_m C_m < \xi_k|H|\xi_i >= E\sum_m < \xi_i|\xi_m > C_m \\ HC = SCE \end{aligned} \tag{3.59}$$

3.6.2 HF MO-LCAO equations using density matrices

We can write HF energy using density matrix:

$$\phi_i = \sum_\mu C_{\mu i}\xi_\mu, \quad \mu = 1\ldots M, i = 1\ldots N$$

$$P_{\mu\nu} = \sum_{i=0}^{n} C_{\mu i}C_{\nu i}$$

$$\begin{aligned} E = \sum_i < i|h|i > +\frac{1}{2}\sum_{ij}(< ij|ij > - < ij|ji >) = \\ \sum_i\sum_{\mu\nu} C_{\mu i}C_{\nu i} < \mu|h|\nu > + \\ \frac{1}{2}\sum_{ij}\sum_{\mu\nu\lambda\sigma} < \mu\nu|\lambda\sigma > C_{\mu i}C_{\nu j}C_{\lambda i}C_{\sigma j} - \\ \frac{1}{2}\sum_{ij}\sum_{\mu\nu\lambda\sigma} < \mu\nu|\sigma\lambda > C_{\mu i}C_{\nu j}C_{\lambda i}C_{\sigma j} = \\ \sum_i\sum_{\mu\nu} C_{\mu i}C_{\nu i} < \mu|h|\nu > + \\ \frac{1}{2}\sum_{ij}\sum_{\mu\nu\lambda\sigma} < \mu\nu||\lambda\sigma > C_{\mu i}C_{\nu j}C_{\lambda i}C_{\sigma j} = \\ Tr[P_{\mu\nu}h_{\mu\nu}] + \\ \frac{1}{2}Tr[P_{\mu\lambda} < \mu\nu||\lambda\sigma > P_{\nu\sigma}] = \\ Tr[Ph + \frac{1}{2}PIIP] \end{aligned} \tag{3.60}$$

$$E = Tr[Ph] + \frac{1}{2}Tr[PIIP] \tag{3.61}$$

$$\frac{\partial E}{\partial P} = F = h + IIP \tag{3.62}$$

3.7 How to solve it?

How to chose an atomic orbital basis? We'll discuss basis sets in details later. The main idea is to take atomic functions from solutions of an atomic problem, i.e., hydrogen-like atomic functions.

Once basis set is chosen, we have to solve somehow a nonlinear system of Roothan equations. It is done by iterative procedure, that's why HF method is often referred to as self-consistent field.

The first step is to take some zero-order (guess) orbitals, C^0. Once we have some set of MO, we can calculate the Fock operator, our effective one-particle Hamiltonian. Once we have a Hamiltonian, how do we minimize the energy of the n-electron wavefunction? As in non-interacting electrons model, we diagonalize the one-particle Hamiltonian and occupy lowest n levels (this is called the Aufbau principle). Note that for interacting electrons the Aufbau Principle does not always work, since $E_{HF} \neq \sum_i \epsilon_i$. Therefore, different electron occupations should be tested.

Those new occupied orbitals (new molecular orbitals, C^1) define new density matrix, new Fockian, and new molecular orbitals from diagonalization of the new Fockian. If new molecular orbitals are the same as old MO's, the equations have been solved. This is a self-consistent procedure:

1. Input: nuclei, electrons & basis set;
2. Make initial guess for MO (e.g., diagonalize h);
3. Make density matrix from MO;
4. Make Fock operator (rate determining step);
5. Diagonalize F;
6. Check whether MO's have converged, i.e., if $|C^n - C^{n-1}| < \epsilon$. If not — go back to step 3.

Actually, such procedure almost never converges. Numerous enhancements are used in practice, i.e., computational methods for many-dimensional optimization (use "gradients" and "Hessians" of the energy with respect to orbital rotations; or DIIS method — extrapolation by using data from previous iterations).

3.7.1 Connection to computation

Memory: need a bunch of matrices (F,H, S, etc) — say 4-8. Mem $\approx 5{*}M^2$, M — basis set size.

Double is 8B. For 126 MB of memory — 18 M doubles ($\approx$ 18,000,000) — $M_{max} \approx 2,000$. How do we connect M_{max} with molecular size? Depend on the basis. In minimal basis set (1 function per atomic orbital) CH_2 has 7 functions in minimal basis, $(CH_2)_{300}$.

Computational part is dominated by Fock matrix computation: F=H+IIP:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} < \mu\nu || \lambda\sigma > P_{\lambda\sigma} \tag{3.63}$$

Cost $\approx$ (# iterations)xM^4x(cost per integral) Cost per integral $\approx$ 100 flop. # of iterations $\approx$ 10-20. Cost $\approx 10^3 - 10^4 * N^4$. For 100 basis functions: $10^{11} - 10^{12}$ adds/mults. For computer 10^7 flops time is 10^4-10^5 seconds (few hours). My computers (2003) — couple of minutes.

3.7.2 Tricks of the trade

1. For very small molecules:

   Use “in core integrals” — compute them once. This reduces cost per iteration to about 10 flops. However, need M^4 memory (actually, $M^4/8$). Often — “on disk integrals”, then IO rate is important.

2. Large molecules:

   Number of non-zero integrals grows as only $O(M^2)$ ($= K^2M^2$), where K is effective # of neighbors. $K \approx 100 - 200$.

3. Very large molecules:

   Linear scaling models (M. Head-Gordon, G. Scuseria groups) (use multipoles, sparsity of density, avoid diagonalization).

PICTURE OF THE COST.
Start see difference for $N \approx 200$

3.7.3 Conclusions

- Large calculations with HF method are feasible
- You now can estimate whether YOUR HF calculation is feasible.

Note: all discussion was about single energy point. But we need at least optimized geometries, etc.

Chapter 4

Basis sets

Why do we use atomic basis set for molecules? Because we know that chemical bonding can be described qualitatively by considering linear combinations of atomic orbitals. Consider H_2 molecule. Wave functions for individual H-atoms are $1s$-functions. From these two orbitals we can prepare two molecular orbitals:

$$\phi_1(r) = \frac{1}{\sqrt{2+s_{AB}}}(1s_A + 1s_B) \equiv \sigma(r) \tag{4.1}$$

$$\phi_2(r) = \frac{1}{\sqrt{2-s_{AB}}}(1s_A - 1s_B) \equiv \sigma^*(r) \tag{4.2}$$

σ is so-called bonding orbital, and σ^* is antibonding orbital. Hartree-Fock wave function for the H_2 is:

$$\Phi_0 = \frac{1}{\sqrt{2}}\sigma(1)\sigma(2)(\alpha\beta - \beta\alpha) \tag{4.3}$$

And this is how Hartree-Fock model describes chemical bonding. We shall discuss H_2 example in more details next time. Now we are concerned about atomic basis sets for electronic structure calculations.

4.1 Atomic orbitals: Slater type orbitals and contracted Gaussians

What do we know about atomic wave functions? For hydrogen-like atom (one electron moving in the Coulomb potential $U(r) = -\frac{Z}{r}$) we can solve the Scarödinger equation analytically:

$$E_n = -\frac{Z^2}{2n^2} \tag{4.4}$$

$$\Phi_{nlm}(r,\theta,\phi) = \exp(-\xi|r|)P_{nl}(r)Y_{lm}(\theta,\phi) \tag{4.5}$$

The energy levels for the hydrogen-like atom are shown in Fig. 4.1.

The radial part of the wave function (4.5) is called Slater type orbital, and its important features are: (i) nuclear cusp; and (ii) asymptotic exponential decay. See Fig. 4.2a.

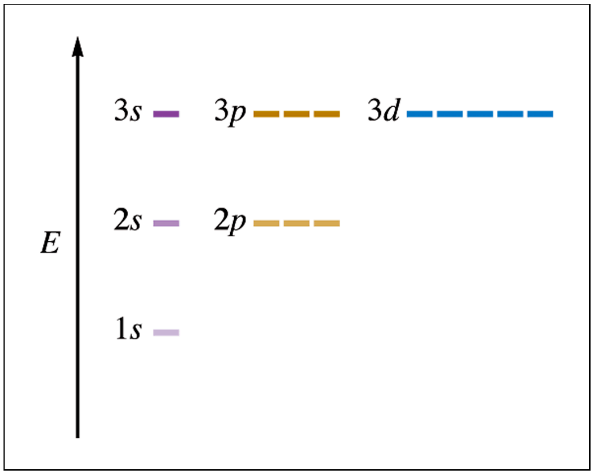


Figure 4.1: Energy levels in hydrogen-like atoms: $E_n = -\frac{Z^2}{2n^2}$. The degeneracy between the levels with the same n but different l is a special feature of the Coulomb potential; it is lifted in other central-symmetric potentials.

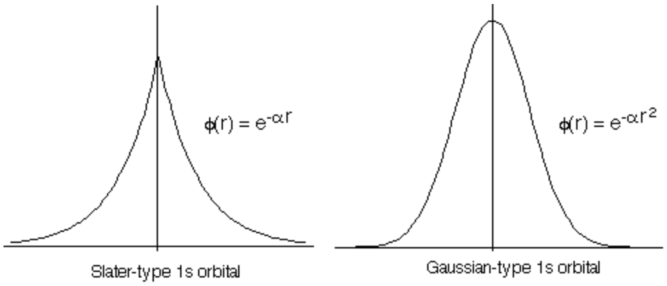


Figure 4.2: Slater-type versus Gaussian-type orbital. Note different shape at r=0 and different asymptotic behavior (at $r \to \infty$). STO exhibits a cusp and a slower decay.

For many electron atoms there is no analytic solution, but asymptotic behavior (cusp and tail) are described correctly by Slater type functions. The structure of energy levels is also similar to those of the hydrogen atoms except for the fact that the degeneracy between levels with same principal quantum number n is removed, and levels with different angular momentum (l) are non-degenerate.

Thus, these hydrogenic atom solutions must be right form for atoms. Then we can mix them together to form molecular orbitals. However, these exponential functions are intractable for practical calculations because we cannot calculate efficiently the 2-electron integrals (six-dimensional integrals). Contrary to Slater type functions, Gaussian functions $1s = e^{-\xi r^2}$ are tractable (because product of two Gaussians is a Gaussian centered in between), but they have (1) wrong shape at nuclei (nuclear cusp) and (2) have too rapid decay at large r. Fig. 4.2 compares STO with GTO.

The solution is to take fixed combination of several Gaussian functions (contractions) to get roughly the right shape (including any radial nodes, etc):

$$\xi_i(r) = \sum_{d=1}^{m} d_{im} e^{-\alpha_m r^2}, \tag{4.6}$$

where ξ_i is an atomic basis function obtained by contraction of m primitive Gaussians, and the coefficients d_{im} are frozen (i.e., not changed in SCF calculations).

STO-3G basis (introduced in 1969) (Slater-type-orbital (modeled by a contraction of) 3 Gaussian functions. STO-3G is called the minimal basis set. In the minimal basis set we take only valence orbitals (1s for H atom, 1s, 2s and 2p for Li atom,

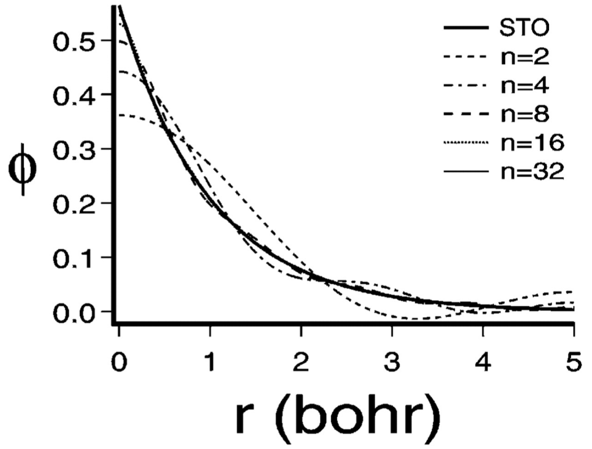


Figure 4.3: Contracted Gaussian functions can approximate STO. The quality of fit can be systematically improved by taking more Gaussians.

etc). This is a minimum required to qualitatively describe chemical bonding. The contraction scheme for STO basis for the C atom is (6s3p)/[2s1p]. A common way of determining contractions is from results of atomic SCF calculations. In these atomic calculations one uses a relatively large basis of uncontracted Gaussians, optimizes all exponents, and determines the SCF coefficients of each of the derived atomic orbitals. Then these exponents are used in primitive Gaussians, and SCF coefficients are used to derive contraction coefficients.

We can improve the description by taking (a) more Gaussians (STO-nG) (actually, 3 is good enough!) (b) more basis functions.

4.2 Extensions

Basis set extensions: what if STO-3G is no good? In order to understand how to improve it, we have to understand what effects it may fail to describe.

4.2.1 Non-isotropic effects: multiple-zeta bases

STO-3G mimics one Slater function with exponent zeta (STO can be called single-zeta basis). Therefore atoms stay isotropic in the molecule. To describe anisotropic effects, we are "splitting the representation": a "double zeta" basis supplies 2 functions (Slater) per atomic orbital called "inner" and "outer". The "inner" AO is slightly less diffuse and the "outer" AO is slightly more diffuse than optimized STO functions. This allows the shape of AO to change upon going to the molecular environment. Example:
HCN: $p_z \to \sigma$ bond
$p_x, p_y \to 2\ \pi$ bonds
π bonds are more diffuse. In σ "inner" orbital has more weight, in π — "outer"

These defines the following sequence of bases sets: Double-Zeta, Triple-Zeta, etc. Many basis sets were developed by Huzinaga and Dunning.

"Split-valence basis" of Pople is essentially the same — except that the core is single zeta (assumes that the core orbitals do not change much upon chemical transformations.

A standard selection of split-valence, DZ basis sets is 3-21G: '3' — minimal core composed of 3 Gaussians; and '-21' — split-valence, valence orbitals are described by inner orbital (composed of two Gaussians) and an outer orbital (composed of 1 Gaussian). The general contraction scheme for carbon is (6s3p)/[3s2p].

You will now understand meaning of 6-31G, 4-31G — there have slightly more Gaussians, but no more contracted functions. Dunning DZ basis (9s5p)/[4s2p] is different from 3-21G.

Triple-zeta: 3 (Slater) orbitals per AO. TZP, 6-311G basis

Also Quadrupole, Pentupole zeta.

It is dangerous, however, to increase only a number of s and p functions. For example, in the limit of a large number of *s* and *p* functions equilibrium geometry of the ammonia become planar. That is because so constructed basis set is not well balanced. What are effects that are omitted in these basis sets? Polarization effects — asymmetric distribution of the electron density around the nuclei in the asymmetric electric field.

4.2.2 Polarized basis sets

Consider atom in an electric field: its electronic density is distorted, and it is no longer possesses spherical symmetry (atom is polarized by an applied field). Atoms in molecules experience influence of an electric field, therefore, we have to account for the polarization effects.

"Polarization functions" are functions of the higher angular momentum and their purpose is to allow polarization of charge. An atomic orbital may be distorted by mixing with a higher angular momentum function:
s+p → "polarized" (distorted, shifted) s-level;
p+d → "polarized" p-level.

We can add higher angular momentum functions to a basis to permit the energy lowering that results from polarization effects.

Cases where polarization is important: (1) bonding in highly polar molecules (NH_3) is a good example (2) strained ring system (C3, discuss hybridization, explain why strained, banana bonds) (3) hypervalency — expanded coordination shells for second row atoms and below (SF_6).

Notations for polarized basis set: 6-31G*, 6-31G**,6-31G(d,p). d describes "heavy" atom polarization, p describes hydrogen atom polarization.

3-21G(*) basis: split valence plus polarization function on second row and below. Similar set of Dunning: DZP.

STO-3G* basis: minimal basis plus polarization function on second row and below.

Caveat: pure angular momentum (5d, 7f, ...) polarization versus Cartesian (6d, 8f, etc).

4.2.3 Diffuse functions

A further split of the valence space to allow a good description of more diffuse charge distribution (appropriate for anions, Rydberg states, electronically excited molecules, van der Waals clusters).

Notations: 6-31+G(*), 6-31++G, 6-311++G(d). '+' means that one set of diffuse orbitals is added to the basis. For H atom this is one diffuse s-orbital, and for second row atoms — one s and one p diffuse orbitals. When two sets of diffuse functions are requested ('2+'), this means that two diffuse s functions are added for hydrogen, and two diffuse s and two diffuse p orbitals are added to second row atoms.

Chapter 5

H_2 example

We shall consider a simple example: H_2 molecule in a minimal basis set. We shall analyze FCI solution (which is an exact solution in the given one electron basis set) and compare it with Hartree-Fock solution. Also, we shall discuss symmetry and spin-symmetry of the wavefunctions by using this simple example.

5.1 Symmetry and spin of an electronic wavefunction

The exact wavefunction must possess proper point group and spin symmetries. Point group symmetry is imposed by a point group symmetry of the external potential, e.g., nuclear potential.

Since non-relativistic Hamiltonian commutes with a spin-operators, they have a set of common eigenstates. Concerning eigenstates of spin operators, we have two operators: S^2 and S_z. Exact wavefunctions are therefore eigenstates of S^2 and S_z:

$$S_z|\sigma>= m_z|\sigma> \tag{5.1}$$

$$S^2|\sigma>= s(s+1)|\sigma>, \tag{5.2}$$

where $|\sigma>$ is a valid spin function, and m_z gives projection of the spin on the z-axis, and s characterizes the absolute value of spin. Term multiplicity (number of states with the same s but different m_z) is given by $\Lambda = 2s + 1$ (because $m_z = -s \dots s$).

However, in a case of approximate non-linear equations, such as HF equations, the approximate wavefunction does not necessarily possess these properties. We can impose proper symmetry by restricting variations of the orbitals, which means that the solution may not be the best in a variational sense. What is better: correct symmetry or best variational solution (Löwdin dilemma)? Hard question... Example: weakly interacting gas and its condensation.

Today we shall consider one- and two- electron spin functions. At home, you shall see that certain conditions must be imposed on the spatial part of the general two-electron Hartree-Fock wavefunction in order to restrict it to the proper spin-symmetry.[1]

---

[1] Restricted HF: S_z, S^2. Orbitals are forced to be the same for α and β electrons: $\{\phi_i(x)\alpha, \phi_i(x)\beta\}$.

5.1.1 One- and two-electron spin functions

One-electron spin functions are just familiar α and β states:

$$|\alpha >= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |\beta >= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{5.3}$$

Cartesian components of one-electron spin operator are given by Pauli matrices:

$$\sigma_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{5.4}$$

Spin-operator, S, is given therefore by a vector composed of Pauli matrices:

$$S = \vec{S} = \vec{e}_x\sigma_x + \vec{e}_y\sigma_y + \vec{e}_z\sigma_z \tag{5.5}$$

Operator S^2 for one electron is just a scalar product of $S \cdot S$:

$$S^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = \frac{3}{4}\hat{E}, \tag{5.6}$$

where $\hat{E}$ is a unit matrix. Operator $S_z = \sigma_z$.

We are interested in wavefunctions which are eigenstates of S_z and S^2. Let us see how S_z and S^2 act on the $|\alpha >$ and $|\beta >$ states:

$$\begin{aligned} S_z\,\alpha = \sigma_z|\alpha >= \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \frac{1}{2}|\alpha > \\ S_z|\beta >= \sigma_z|\beta >= \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} &= -\frac{1}{2}|\beta > \\ S^2|\alpha > &= \frac{3}{4}|\alpha > \\ S^2|\beta > &= \frac{3}{4}|\beta > \end{aligned} \tag{5.7}$$

Thus, $|\alpha >$ and $|\beta >$ are eigenstates of S_z with an eigenvalues $\frac{1}{2}$ and $-\frac{1}{2}$, respectively, and eigenstates of S^2 with an eigenvalue of $\frac{3}{4}$.

We shall also need to know how operators σ_x and σ_y act on α and β functions:

$$\sigma_x|\alpha >= \frac{1}{2}|\beta > \tag{5.8}$$

$$\sigma_x|\beta >= \frac{1}{2}|\alpha > \tag{5.9}$$

$$\sigma_y|\alpha >= \frac{i}{2}|\beta > \tag{5.10}$$

$$\sigma_y|\beta >= -\frac{i}{2}|\alpha > \tag{5.11}$$

$$\tag{5.12}$$

Unrestricted HF: S_z is ok, S^2 — not. Orbitals may differ for α and β electrons: $\{\phi_i(x)\alpha, \psi_i(x)\beta\}$. General HF: S_z, S^2 — not. Orbitals are complex and assumes a most general form: $\{\phi_i(x)\alpha + \psi_i(x)\beta\}$

How do we construct two-electron wavefunctions and operators? Wavefunctions are given by a linear combinations of products of α and β. We shall find what combinations are legal. Two-electron spin operators are given by a sum of one-electron operators:

$$\vec{S}(1,2) = \vec{S}(1) + \vec{S}(2) \tag{5.13}$$

$$S_z(1,2) = S_z(1) + S_z(2) \tag{5.14}$$

$$S^2(1,2) = \left[\vec{S}(1) + \vec{S}(2)\right]^2 = \tag{5.15}$$

$$S^2(1) + S^2(2) + 2\vec{S}(1)\cdot\vec{S}(2) = \tag{5.16}$$

$$\frac{3}{2}\hat{E} + 2\left[\sigma_x(1)\sigma_x(2) + \sigma_y(1)\sigma_y(2) + \sigma_z(1)\sigma_z(2)\right] \tag{5.17}$$

Let us consider now the following two-electron wavefunctions: $\alpha(1)\cdot\alpha(2)$, $\beta(1)\cdot\beta(2)$, and $\alpha(1)\cdot\beta(2)$.

Applying S_z to $\alpha(1)\cdot\alpha(2)$:

$$\begin{aligned} S_z(1,2)\Big[\alpha(1)\cdot\alpha(2)\Big] &= \\ \alpha(2)\cdot\Big[s_z(1)\alpha(1)\Big] + \alpha(1)\cdot\Big[s_z(2)\alpha(2)\Big] &= \\ 1\cdot[\alpha(1)\cdot\alpha(2)] \end{aligned} \tag{5.18}$$

Applying S^2 to $\alpha(1)\cdot\alpha(2)$:

$$\begin{aligned} S^2(1,2)\Big[\alpha(1)\cdot\alpha(2)\Big] = \frac{3}{2}\hat{E}\Big[\alpha(1)\cdot\alpha(2)\Big] + 2\Big[\sigma_x(1)\alpha(1)\Big]\cdot\Big[\sigma_x(2)\alpha(2)\Big] &+ \\ 2\Big[\sigma_y(1)\alpha(1)\Big]\cdot\Big[\sigma_y(2)\alpha(2)\Big] + 2\Big[\sigma_z(1)\alpha(1)\Big]\cdot\Big[\sigma_z(2)\alpha(2)\Big] &= \\ \frac{3}{2}\cdot\Big[\alpha(1)\cdot\alpha(2)\Big] + 2\cdot\frac{1}{4}\cdot\Big\{\beta(1)\cdot\beta(2) + (-1)\beta(1)\cdot\beta(2) + \alpha(1)\cdot\alpha(2)\Big\} &= \\ 2\cdot[\alpha(1)\cdot\alpha(2)] \end{aligned} \tag{5.19}$$

Conclusion: $\alpha(1)\cdot\alpha(2)$ *is* an eigenfunction of the operators S_z and S^2 and its eigenvalues are respectively 1 and 2. Since $2 =< S^2 >= s(s+1)$, it follows that $s = 1$. The term multiplicity is defined as $\Lambda = 2s+1$ and is equal to 3. Similarly, $\beta(1)\cdot\beta(2)$ is an eigenfunction of the operators S_z and S^2 and their eigenvalues are respectively -1 and 2. Since $2 =< S^2 >= s(s+1)$, it follows that $s = 1$. The term multiplicity is 3.

Applying S_z to $\alpha(1)\cdot\beta(2)$:

$$\begin{aligned} S_z(1,2)\Big[\alpha(1)\cdot\beta(2)\Big] = \beta(2)\cdot\Big[\sigma_z(1)\alpha(1)\Big] + \alpha(1)\cdot\Big[\sigma_z(2)\beta(2)\Big] &= \\ \alpha(1)\cdot\beta(2) - \alpha(1)\cdot\beta(2) = 0\cdot[\alpha(1)\cdot\beta(2)] \end{aligned} \tag{5.20}$$

Applying S^2 to $\alpha(1)\cdot\beta(2)$:

$$S^2(1,2)\Big[\alpha(1)\cdot\beta(2)\Big] = \frac{3}{2}\hat{E}\Big[\alpha(1)\cdot\beta(2)\Big] + 2\Big[\sigma_x(1)\alpha(1)\Big]\cdot\Big[\sigma_x(2)\beta(2)\Big] +$$

$$\begin{gathered}2\Big[\sigma_y(1)\alpha(1)\Big]\cdot\Big[\sigma_y(2)\beta(2)\Big]+2\Big[\sigma_z(1)\alpha(1)\Big]\cdot\Big[\sigma_z(2)\beta(2)\Big]=\\ \frac{3}{2}\cdot\Big[\alpha(1)\cdot\beta(2)\Big]+2\cdot\frac{1}{4}\cdot\Big\{\beta(1)\cdot\alpha(2)+i\beta(1)\cdot(-i)\alpha(2)+\alpha(1)\cdot(-1)\beta(2)\Big\}=\\ =[\alpha(1)\cdot\beta(2)]+[\beta(1)\cdot\alpha(2)]\end{gathered} \tag{5.21}$$

Conclusion: $\alpha(1)\cdot\beta(2)$ *is* an eigenfunction of the operator S_z. The eigenvalue is 0. $\alpha(1)\cdot\beta(2)$ *is not* an eigenfunction of the operator S^2. We can calculate the expectation value of $< S^2 >$:

$$\begin{gathered}< S^2 >=< \alpha(1)\cdot\beta(2)|S^2|\alpha(1)\cdot\beta(2) >=\\ < \alpha(1)\cdot\beta(2)|\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2) >= 1\end{gathered} \tag{5.22}$$

Similarly, $\beta(1)\cdot\alpha(2)$ is an eigenfunction of S_z and is not an eigenfunction of S^2. We can consider linear combinations $\frac{1}{\sqrt{2}}(\alpha\beta \pm \beta\alpha)$.

Applying S_z to $\frac{1}{\sqrt{2}}[\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2)]$:

$$S_z(1,2)\frac{1}{\sqrt{2}}\Big[\alpha(1)\cdot\alpha(2)+\beta(1)\cdot\alpha(2)\Big]=0\cdot\Big[\alpha(1)\cdot\alpha(2)+\beta(1)\cdot\alpha(2)\Big]$$

Applying S^2 to $\frac{1}{\sqrt{2}}[\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2)]$:

$$S^2(1,2)\frac{1}{\sqrt{2}}\Big[\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2)\Big]=2\cdot\Big[\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2)\Big]$$

Conclusion: $\frac{1}{\sqrt{2}}[\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2)]$ *is* an eigenfunction of the operators S_z and S^2 with eigenvalues are respectively 0 and 2. s is 1, and multiplicity equals 3.

Applying S_z to $\frac{1}{\sqrt{2}}[\alpha(1)\cdot\beta(2)-\beta(1)\cdot\alpha(2)]$:

$$S_z(1,2)\frac{1}{\sqrt{2}}\Big[\alpha(1)\cdot\alpha(2)-\beta(1)\cdot\alpha(2)\Big]=0\cdot\Big[\alpha(1)\cdot\alpha(2)-\beta(1)\cdot\alpha(2)\Big]$$

Applying S^2 to $\frac{1}{\sqrt{2}}[\alpha(1)\cdot\beta(2)-\beta(1)\cdot\alpha(2)]$:

$$S^2(1,2)\frac{1}{\sqrt{2}}\Big[\alpha(1)\cdot\beta(2)-\beta(1)\cdot\alpha(2)\Big]=0\cdot\Big[\alpha(1)\cdot\beta(2)+\beta(1)\cdot\alpha(2)\Big]$$

Conclusion: $\frac{1}{\sqrt{2}}[\alpha(1)\cdot\beta(2)-\beta(1)\cdot\alpha(2)]$ *is* an eigenfunction of the operators S_z and S^2 with eigenvalues 0 and 0, respectively. $s = 0$ and the term multiplicity $\Lambda = 1$.

To summarize, Table 5.1 gives valid spin-functions for two electrons.

Note that multiplicity can define spatial symmetry. Triplet functions are symmetric with respect to electron permutations, hence, must be combined with an antisymmetric spatial part. Singlets are antisymmetric, should be combined with symmetric spatial part.

Table 5.1: Valid two-electron spin-functions

	S_z	$< S^2 >= s(s+1)$	Multiplicity $\Lambda = (2s+1)$
$\alpha(1)\alpha(2)$	1	2	3 (triplet)
$\beta(1)\beta(2)$	-1	2	3 (triplet)
$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$	0	2	3 (triplet)
$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$	0	0	1 (singlet)

5.2 H_2: Hartree-Fock wavefunction

We have two atoms: H_A & H_B. In a minimal basis set there are two 1s orbitals centered on each atom: $1s_A$ & $1s_B$.

Here we shall *restrict* our HF wavefunction to be of correct symmetry. This leads to *restricted* HF (usually it means spin-restricted HF, a model when HF wavefunction has correct spin symmetry).

General HF solution would be:

$$
\begin{gathered}
|\Phi(1,2) >= |\phi_1\phi_2 >= \\
\frac{1}{\sqrt{2}}\begin{pmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{pmatrix},
\end{gathered}
\tag{5.23}
$$

where ϕ_1, ϕ_2 can have any kind of spin or spatial part

If we require correct spin symmetry, we end up in forcing each orbital to have a pure spin (α or β, but not a mixture), and spatial parts to be the same for α and β spin-orbitals.

Such, for singlet function we end up with:

$$
\begin{aligned}
|\Phi^{RHF}(1,2) >= |\phi\alpha\ \phi\beta >= \\
\frac{1}{\sqrt{2}}\begin{pmatrix} \phi(1)\alpha(1) & \phi(1)\beta(1) \\ \phi(2)\alpha(2) & \phi(2)\beta(2) \end{pmatrix} = \\
\frac{1}{\sqrt{2}}(\phi(1)\phi(2)\alpha(1)\beta(2) - \\
\phi(2)\phi(1)\beta(1)\alpha(2)) = \\
\frac{1}{\sqrt{2}}\phi(1)\phi(2) * [\alpha(1)\beta(2) - \beta(1)\alpha(2)]
\end{aligned}
\tag{5.24}
$$

What is that? Properly anti-symmetrized doubly occupied orbital ϕ, with a singlet spin function.

What can ϕ be for H_2? Most general form:

$$
\begin{gathered}
\phi = c_1 s_A + c_2 s_B \\
c_1^2 + c_2^2 + 2c_1c_2 < s_a|s_b >= 1
\end{gathered}
\tag{5.25}
$$

For this particular case there is no need to solve HF equations to find coefficients c_1 and c_2 if we require wavefunction to have correct symmetry.

Consider now spatial symmetry of that wavefunction. Point group is $C_{\infty v}$. For the minimal basis set we can disregard symmetry associated with rotations and the plane (1s functions are symmetric). The non-trivial symmetry element is an inversion center i. Wavefunction should be either gerade or ungerade symmetry. For $\phi_1(1)\phi_2(2)$ wavefunction that means that orbitals ϕ_1 and ϕ_2 should have either gerade or ungerade symmetry.

This means that we have restriction on coefficients c_i: $c_1 = \pm c_2$ This results in two orthogonal MO's (we skip normalization factor of $\frac{1}{\sqrt{2(1\pm<s_A|s_B>)}}$):

$$\begin{aligned} \sigma &= (s_A + s_B) \\ \sigma^* &= (s_A - s_B) \end{aligned} \tag{5.26}$$

Orbital σ is gerade, σ^* — ungerade. Wavefunctions: $\sigma(1)\sigma(2)$, $\sigma^*(1)\sigma^*(2)$ are gerade; $\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)$, $\sigma(1)\sigma^*(2) + \sigma^*(1)\sigma(2)$ are ungerade.

Energy of orbital σ is lower than that of σ^* We can see it from nodes. Or derive from integrals. Energy gap depends on overlap. For small distances, it is large. For large distances, when two-center integrals and overlap are zero, σ and σ^* are degenerate.

That in conjunction with Aufbau principle gives for HF solution:

$$|\Phi_0 >= \frac{1}{\sqrt{2}}\sigma(1)\sigma(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \tag{5.27}$$

We can also show that HF energy of σ^2 is lower than energy of $(\sigma^*)^2$ (when orbitals are not degenerate). Orbital σ is called bonding orbital, orbital σ^* — antibonding. Chemical bond formation: electronic density between atoms. Differential density. (Do at home).

5.2.1 Analysis of Hartree-Fock wavefunction

Now lets analyze spatial part of Φ_0:

$$\begin{aligned} \Phi_0 = \sigma\sigma = (s_A + s_B)(s_A + s_B) = \\ s_A s_A + s_B s_B + s_A s_B + s_B s_A = \\ H_A^- H_B^+ + H_A^+ H_B^- + H_A H_B + H_A H_B \end{aligned} \tag{5.28}$$

Configurations $H_A^- H_B^+$ and $H_A^+ H_B^-$ are ionic: they describe situation when both electrons are localized near one of the H-atoms (there is unit probability to find both electrons near one H-atom).

Configuration $H_A H_B$ is covalent: it describes situation when one electron is localized near one of the H-atoms, and second electron is localized near another H-atom (there is unit probability to find electrons near different atoms).

Φ_0 alone is a mixture of ionic and covalent configurations in a fixed proportion. We have no variational freedom to vary degree of ionicity in HF wavefunction.

Conclusions:

- can be wrong for strongly ionic/strongly covalent situation;
- cannot describe ether neutral ($H_2 \to H + H$), or ionic ($H_2 \to H^+ + H^-$) dissociation.

This is very important limitation of the Hartree-Fock model: it cannot describe chemical bond breaking.

5.2.2 Unrestricted Hartree-Fock wavefunction

What if we do not impose correct symmetry on the Hartree-Fock wavefunction? The resulting model is called *unrestricted* Hartree-Fock. In this model we do not apply any restrictions on Φ_0 — just looking for the lowest energy solution. In (spin) unrestricted HF orbitals for α and β electrons are different. As a result, Φ_0 is eigenstate of S_z, but not an eigenstate of S^2.

For the H_2 molecule at the dissociation limit we have:

$$\begin{aligned} \Phi_0^{UHF}(r \to \infty) = |s_A \alpha s_B \beta >= \\ \frac{1}{\sqrt{2}} \begin{pmatrix} s_A(1)\alpha(1) & s_B(1)\beta(1) \\ s_A(2)\alpha(2) & s_B(2)\beta(2) \end{pmatrix} = \\ \frac{1}{\sqrt{2}}(s_A(1)\alpha(1)s_B(2)\beta(2) - \\ s_B(1)\beta(1)s_A(2)\alpha(2)) \end{aligned} \tag{5.29}$$

This wavefunction does describe covalent dissociation (it does not have any ionic contributions in it). However, it does not possess proper symmetry. This wavefunction is an eigenstate of S_z, but not an eigenstate of S^2. We can calculate expectation value for S^2: $< S^2 >=1$, meaning that such wavefunction is a mixture of singlet ($< S^2 >=0$) and triplet ($< S^2 >=2$) states. It is said to be spin-contaminated. Spin-contamination means that approximate wavefunction does not give $< S^2 >$ corresponding to the pure spin-cases.

We can see that unrestricted HF wavefunction is a mixture of singlet and triplet by considering linear combination of covalent singlet and covalent triplet wavefunctions:

$$\begin{aligned} \Psi_{cov}^{singlet} &= (s_A s_B + s_B s_A)(\alpha\beta - \beta\alpha) = \\ &\quad (s_A \alpha s_B \beta - s_B \beta s_A \alpha) + \\ &\quad (s_B \alpha s_A \beta - s_A \beta s_B \alpha) \\ \Psi_{cov}^{triplet} &= (s_A s_B - s_B s_A)(\alpha\beta + \beta\alpha) = \\ &\quad (s_A \alpha s_B \beta - s_B \beta s_A \alpha) + \\ &\quad (s_A \beta s_B \alpha - s_B \alpha s_A \beta) \\ \Psi_0^{UHF} &= \frac{1}{\sqrt{2}}(\Psi_{cov}^{singlet} + \Psi_{cov}^{triplet}) \end{aligned} \tag{5.30}$$

Φ_0^{UHF} is a mixture of singlet and triplet. Singlet and triplet are degenerate at the dissociation limit, so energetically UHF is better that RHF. However, the lack of proper symmetry is very serious problem.

Note that in this case UHF wavefunction does not have correct spatial symmetry: it is a mixture of gerade and ungerade functions.

Spin-contamination may occur not only at dissociation limit, but also at equilibrium. One of the examples: HF for radicals.

PICTURE of alpha and beta MO's here

Two models are available: UHF and ROHF. For UHF calculations one has to analyze what is $< S^2 >$. For doublet radicals it should be 0.75. If it is much different from that — you have to be very cautious about the results. ROHF — not necessarily better... Radicals are more problematic for HF theory than closed-shell molecules.

5.3 H_2: an exact solution in the minimal basis set

Let us construct now a multi-electron basis set for H_2, and analyze FCI wavefunction.

Consider single excitations:

Excitation $\sigma\beta \to \sigma^*\alpha$:

$$\begin{aligned} \Phi_{\sigma\beta}^{\sigma^*\alpha} = |\sigma\alpha, \sigma^*\alpha >= \\ \frac{1}{\sqrt{2}} \begin{pmatrix} \sigma(1)\alpha(1) & \sigma^*(1)\alpha(1) \\ \sigma(2)\alpha(2) & \sigma^*(2)\alpha(2) \end{pmatrix} = \\ \frac{1}{\sqrt{2}} \left(\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\right) \alpha(1)\alpha(2) \end{aligned} \tag{5.31}$$

This is a triplet state (pure spin state).

Similarly, excitation $\sigma\alpha \to \sigma^*\beta$:

$$\begin{aligned} \Phi_{\sigma\alpha}^{\sigma^*\beta} = |\sigma\beta, \sigma^*\beta >= \\ \frac{1}{\sqrt{2}} \left(\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\right) \beta(1)\beta(2) \end{aligned} \tag{5.32}$$

Excitation $\sigma\beta \to \sigma^*\beta$:

$$\begin{aligned} \Phi_{\sigma\beta}^{\sigma^*\beta} = |\sigma\alpha, \sigma^*\beta >= \\ \frac{1}{\sqrt{2}} \begin{pmatrix} \sigma(1)\alpha(1) & \sigma^*(1)\beta(1) \\ \sigma(2)\alpha(2) & \sigma^*(2)\beta(2) \end{pmatrix} = \\ \frac{1}{\sqrt{2}}(\sigma(1)\sigma^*(2)\alpha(1)\beta(2) - \\ \sigma^*(1)\sigma(2)\beta(1)\alpha(2)) \end{aligned} \tag{5.33}$$

This is not a pure spin state (is not an eigenstate of $\hat{S}^2$).

Similarly, excitation $\sigma\alpha \to \sigma^*\alpha$

$$\Phi_{\sigma\alpha}^{\sigma^*\alpha} = |\sigma\beta, \sigma^*\alpha >=$$

$$\frac{1}{\sqrt{2}}\begin{pmatrix}\sigma(1)\beta(1) & \sigma^*(1)\alpha(1)\\ \sigma(2)\beta(2) & \sigma^*(2)\alpha(2)\end{pmatrix} = \frac{1}{\sqrt{2}}(\sigma(1)\sigma^*(2)\beta(1)\alpha(2) - \sigma^*(1)\sigma(2)\alpha(1)\beta(2)) \tag{5.34}$$

This is not a pure spin state (is not an eigenstate of $\hat{S}^2$).

We can take linear combination of two last determinants:

$$\Phi_{\sigma\beta}^{\sigma^*\beta} + \Phi_{\sigma\alpha}^{\sigma^*\alpha} = \frac{1}{\sqrt{2}}\left(\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\right)\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right) \tag{5.35}$$

$$\Phi_{\sigma\beta}^{\sigma^*\beta} - \Phi_{\sigma\alpha}^{\sigma^*\alpha} = \frac{1}{\sqrt{2}}\left(\sigma(1)\sigma^*(2) + \sigma^*(1)\sigma(2)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right) \tag{5.36}$$

Note that first linear combination is a pure triplet function (with $< S_z >=0$), whereas second is a pure singlet.

As a consequence of Pauli principle, spatial part of triplets is antisymmetric with respect to electron interchange. Spatial part of singlets is symmetric.

Can last singlet be present in FCI wavefunction? No, because of symmetry considerations. It is of ungerade symmetry (gxu=u), when HF determinant is gerade.

FCI wavefunction:

$$\Psi_{FCI} = C_0\Phi_0 + C_1\Phi_1, \tag{5.37}$$

where

$$\Phi_0 = \sigma\sigma\left[\alpha\beta - \beta\alpha\right] \tag{5.38}$$

$$\Phi_2 = \sigma^*\sigma^*\left[\alpha\beta - \beta\alpha\right] \tag{5.39}$$

At equilibrium, when there is an energy gap between σ and σ^*, Φ_0 has energy much lower than Φ_2, and C_0 is large.

At large r_{AB}, when σ and σ^* are degenerate, coefficients C_0 and C_1 are of the same magnitude.

As we have shown in the previous section, Φ_0 is a mixture of the ionic and covalent configurations in a fixed proportion:

$$\Phi_0 = \sigma\sigma = (s_A + s_B)(s_A + s_B) = s_As_A + s_Bs_B + s_As_B + s_Bs_A = H_A^-H_B^+ + H_A^+H_B^- + H_AH_B + H_AH_B \tag{5.40}$$

Similarly, Φ_2 is given by:

$$\Phi_2 = \sigma\sigma = (s_A - s_B)(s_A - s_B) = s_As_A + s_Bs_B - s_As_B - s_Bs_A = H_A^-H_B^+ + H_A^+H_B^- - H_AH_B - H_AH_B \tag{5.41}$$

Therefore, FCI has enough variational freedom to describe both ionic and covalent dissociation by mixing these two configurations:

$$\begin{aligned} \Phi_0 - \Phi_2 &= H_A H_B + H_B H_A \\ \Phi_0 + \Phi_2 &= H_A^+ H_B^- + H_A^- H_B^+ \end{aligned} \tag{5.42}$$

Chapter 6

Qualitative molecular orbital theory

From the H_2 example, we now understand how the Hartree-Fock model describes bonds in molecules: additional stabilization (w.r.t. individual fragments) is achieved by “sharing” the electrons which occupy molecular bonding orbitals (which have more density between the atoms).

It is possible to generalize many of the HF results in a qualitative picture which can be used to analyze bonding. There are numerous variants of such qualitative (or even semi-quantitative) models. I am going to discuss the simplest variant and give you examples of how it can be used.

Qualitative molecular orbital theory rules:

1. MOs are formed only from AOs which are close in energy.
2. Two interacting AOs form bonding (lower energy, no node between fragments) and anti-bonding (higher energy, node) pair.
3. Bonding-antibonding splitting is proportional to the overlap between AOs and is zero when overlap is zero.
4. Overlap (and thus bonding-antibonding splittings) decrease in the following sequence of MOs : $\sigma \rightarrow \pi \rightarrow \delta \ldots$
5. Bond energy (or stabilization energy w.r.t. fragments) is roughly equal to one-electron energies (sum of energies of occupied MOs) minus small electron repulsion (which only becomes important when orbitals are degenerate or nearly degenerate).
6. Bond order equals $\frac{1}{2}(N_{electrons-on-bonding-orbitals} - N_{electrons-on-anti-bonding-orbitals})$.

Related very useful qualitative tool: Hückel theory.

Examples:

1. O_2 molecule: consider MOs, calculate bond order, define multiplicity. Relative stability of the neutral, cation, and anion.

2. CH_2Cl radical.[14,15] Bond contraction relative to saturated compound, anomalous charge distributions. Excited states and their properties: lowest valence ($\pi^* \rightarrow \sigma^*$ transition) and Rydberg states.

3. Why weakly bound covalent dimers are so weakly bound? Bond formed by anti-bonding orbitals: NO and $(NO)_2$. Mention multi-reference character.

4. Al-ethylene dimer: covalently bound vs. van der Waals.[16]

5. Ethylene and twisted ethylene. Covalent nature of triplets. Singlet states.

Chapter 7

Performance of Hartree-Fock theory

Notation for a model chemistry: correlation treatment/basis set (correlation approximation/algebraic approximation — basis set truncation).

Hence, our first model is HF/STO-3G. There are two approaches how to obtain believable results form our calculations.

- for our molecule, apply a series of improved models until converged results are obtained: "molecule at a time approach";
- for a given theoretical model, understand how it treats a whole range of chemical problems, and it will then acquire some predictive credibility.

The second approach is more powerful, as it permits us to study trends in a natural way. We have already discussed these ideas in the beginning, when talking about *ab initio* "error bars", predictability, and calibration of approximate models.

We will test performance of HF theory for:

1. Optimized molecular geometries (AH_n, ABH_n, first row atoms, second row atoms);
2. Vibrational frequencies;
3. Relative energies:
    - internal rotation;
    - bond dissociation energies;
    - transition states;
    - isogyric reactions (conserve number of electron pairs);
    - isodesmic reaction (conserve number of bonds of the same type).

7.1 Geometries

Geometry optimization for closed shell, neutral molecules. Consider the sequence STO-3G → 3-21G → 6-31G*, i.e., single-zeta → double-zeta → double-zeta with polarization.

7.1.1 AH_n molecules

Molecules: H_2, LiH, CH_4, NH_3, H_2O, HF, NaH, SiH_4, PH_3, H_2S, HCl. Total: 21 bond lengths, 8 angles. Results are in Table 7.1.

Table 7.1: Results for the 11 AH_n molecules

Basis	$< \lvert r_{calc} - r_{exp} \rvert >$, Å
STO-3G	0.060
3-21G	0.016
6-31G*	0.014

7.1.2 AH_nBH_m molecules

Consider AB bonds:

1. STO-3G:
   - single bonds involving C are quite good (0.02-0.03 Å);
   - Single bonds between other elements show much larger errors;
   - Multiple bonds not well described;
   - Overall $< \lvert r_{calc} - r_{exp} \rvert >$=0.082Å.
2. 3-21G:
   - Multiple bonds better described;
   - Single bonds not uniformly improved;
   - Overall $< \lvert r_{calc} - r_{exp} \rvert >$=0.067Å.
3. 6-31G*:
   - Generally improved results except for bonds between electropositive elements (first row atoms);
   - Multiple bonds slightly underestimated (0.01-0.02 Å);
   - Overall estimate for accuracy for organic molecules approaches 0.01Å, 1^o.

Table 7.2: Overall results for polyatomics. (An average error in Å).

Basis	Single bond	Multiple bond	All bonds
STO-3G	0.030	0.027	0.029
3-21G	0.033	0.019	0.029
3-21G*	0.015	0.018	0.016
6-31G*	0.020	0.021	0.020

7.1.3 Overall results for polyatomics

Overall results for polyatomics are in Table 7.2. Examples for specific molecules are given in Table 7.3.

Is error a systematic? Not quite. In a Hartree-Fock limit — generally underestimated bond length. Why underestimates? HF is too ionic. Why STO — overestimates? No polarization. Angles change correspondingly.

Table 7.3: Composed table from Szabo (bond lengths are in bohr).

Basis	H_2	N_2	CO	CH_4	NH_3	H_20	FH
STO-3G	1.346	2.143	2.166	2.047	1.952	1.871	1.807
4-31G	1.380	2.050	2.132	2.043	1.873	1.797	1.742
6-31G*		2.039	2.105	2.048	1.897	1.791	1.722
6-31G**	1.385			2.048	1.897	1.782	1.703
NHFL		2.013	2.081	2.048	1.890	1.776	1.696
Exp	1.401	2.074	2.132	2.050	1.912	1.809	1.733

Hyper-valent molecules: PF_5, SF_6, $FClO_2$, $FClO_3$ (results in Table 7.4).

Table 7.4: Hypervalent molecules: PF_5, SF_6, $FClO_2$, $FClO_3$.

Basis	$< \lvert r_{calc} - r_{exp} \rvert >$
STO-3G	0.125
3-21G*	0.015
6-31G*	0.014

Overall: HF theory with DZ or DZP basis is quite accurate (0.01-0.02Å, 1-2^o) for compounds with 1st and 2nd row atoms. Basis set convergence is *fast*.

7.2 Harmonic vibrational frequencies

STO-3G generally very poor — we shall not study it further. Results are in Table 7.5. Comparison with the experiment is difficult, because experimental data include *anharmonicity*, which tends to make results lower than if only the harmonic part of the potential was used (see Fig. 7.1).

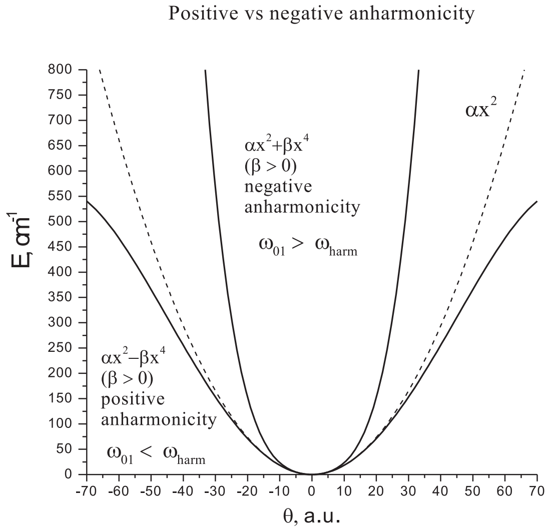

Positive vs negative anharmonicity

Figure 7.1: Harmonic and anharmonic potentials. All three potentials have identical harmonic part. Positive anharmonicity (i.e., $\omega_{01} < \omega_{harm}$) is common in stretching vibrations. Negative anharmonicity (i.e., $\omega_{01} > \omega_{harm}$) may occur in bending, torsional, and out-of-plane vibrations.

Table 7.5: Vibrational frequencies.

	Basis	$\Delta\nu$, %
AH$_n$	3-21G	7.1
	6-31G*	8.0
AH$_n$BH$_n$	3-21G	12.8
	6-31G*	13.0

3-5% of the error may be anharmonicity. What do these percents mean? For ν=1500cm^{-1} (C-C bond) 1% means 15 cm^{-1}. Error is *systematic*, not random. Frequencies are too high. Overall: $\Delta\nu(3-21G) \approx \Delta\nu(6-31G*)$=11% larger then observed. Hence, can scale by 0.9 to empirically correct. This helps to calculate reliable zero-point energies in particular.

Why larger? HF is too ionic, bond strength is overestimated.

7.3 Relative energies

7.3.1 Internal rotation

Generally quite successful, because no bonds are made or broken (error cancellation). 6-31G* is needed for reasonable treatment of conjugated molecules.

7.3.2 Bond strength

Generally a disaster.

Cannot do directly — from H_2 example must be clear that we cannot describe dissociation curves & transition states.

Can do indirectly, by calculating energy differences: calculate AB, then separately A and B and not non-interacting A B.

AH bond energies: $\Delta E \approx$ 24-40 kcal/mol $\approx$ 1-2 eV For the reference: typical AH bond strength $\approx$ 100 kcal/mol $\approx$ 5 eV.

AB bond strength: similarly, but errors are larger for all basis sets, up to 50 kcal/mol.

Why so bad? Hydrogenation energies: slightly better (closed shell reactions).

7.3.3 Isogyric & isodesmic reactions

The origin of the worst failure we have seen in bond strength is not in the basis set: it is neglect of *electron correlation* due to making Hartree-Fock approximation. Correlation is largest for electrons close together. Hence, in bond breaking process — use isogyric reactions (conserve # of electron pairs).

Example: C-H bond strength.

Reaction

$$CH_4(^1A_1) \rightarrow CH_3(^2A_2^{''}) + H(^2S) \tag{7.1}$$

is non-isogyric.

Reaction

$$CH_4(^1A_1) + H(^2S) \rightarrow CH_3(^2A_2^{''}) + H_2(^1\Sigma_g^+) \tag{7.2}$$

is isogyric.

Then can try to balance the chemistry more closely between left and right sides of a reaction.

Isodesmic reactions: conserve # of bonds of each formal type — only alter their connectivity.

Examples:

1. internal rotation;
2. many problems involving relative energetics of isomers;
3. bond separation reactions — separate all heavy atom linkages into 2 atom parents, balancing with 1 atom hydrides;

   Example:

$$\begin{aligned} CH_3 - CH = C = O + 2CH_4 \rightarrow CH_3 - CH_3 + \\ CH_2 = CH_2 + CH_2 = O \end{aligned} \tag{7.3}$$

   even STO-3G is OK for molecules with a single dominant valence structure;

4. heats of formation: combine known results with isodesmic reactions to predict unknowns.

Example: isomerization energy of $CH_3CH_2OH \rightarrow CH_3OCH_3$. Can be calculated directly (this is isogyric reaction), or by isodesmic reactions as follows:

$$\begin{aligned} CH_3CH_2OH + CH_4 \rightarrow \\ CH_3CH_3 + CH_3OH + BSE(CH_3CH_2OH) \end{aligned} \tag{7.4}$$

$$\begin{aligned} \Delta H(CH_3CH_2OH) = \Delta H(CH_3CH_3) + \Delta H(CH_3OH) - \\ \Delta H(CH_4) - BSE(CH_3CH_2OH) \end{aligned} \tag{7.5}$$

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH + BSE(CH_3OCH_3) \tag{7.6}$$

$$\begin{aligned} \Delta H(CH_3OCH_3) = 2\Delta H(CH_3OH) - \\ \Delta H(H_2O) - BSE(CH_3OCH_3) \end{aligned} \tag{7.7}$$

Note: isomerization energy of $CH_3CH_2OH \rightarrow CH_3OCH_3$ is then much better predicted than by the direct (isogyric) energy difference, especially with small basis sets.

$$\begin{aligned} \Delta E = \Delta H(CH_3OCH_3) - \Delta H(CH_3CH_2OH) = \\ \Delta H(CH_3OH) - \Delta H(H_2O) \\ -\Delta H(CH_3CH_3) + \Delta H(CH_4) \\ -BSE(CH_3OCH_3) + BSE(CH_3CH_2OH) \end{aligned} \tag{7.8}$$

The trick is general, can be used with more advanced methods.

To conclude: while we can use simple tricks like isodesmic reactions to “dodge the bullet” of electron correlation in some cases, it is also clear that we simply cannot get away with Hartree-Fock theory in general, especially for molecules with non-classical structures. We must look into the problem of electron correlation.

7.4 Conclusions

1. Energy point: Scaling: N^4. Memory: N^2. Linear scaling models. Rather feasible. Gradients and frequencies are more expensive.

2. Accuracy?

   - Geometries: HF theory with DZ or DZP basis is quite accurate (0.01-0.02Å, 1-2^o) for compounds with 1st and 2nd row atoms.

- Frequencies: $\Delta\nu(3-21G) \approx \Delta\nu(6-31G*) = 11\%$. Error is systematic, can use scaling.
- Energetics:
  - internal rotation: OK;
  - bond strength — disaster (1-2) eV (for 5 eV AH bonds), and larger;
  - dissociation and transition states — disaster;
  - isogyric reactions — OK;
  - isodesmic reactions — OK;
  - When breaks: multireference, bond-breaking problem, radicals, diradicals.

3. Predictive: yes.
4. Size-extensive: yes (for two closed-shell fragments); (Size-consistent: no).
5. Variational: yes.

Chapter 8

Reduced density matrices and electronic density

Reduced density matrices are very important in electronic structure since they (i) allow for compressing information; (ii) are used to for wave function analysis; (iii) some results can be written in a general form using density matrices, i.e., independent on the ansatz we use.

8.1 Density matrices

Consider $\Psi(1, \ldots, N)$ normalized anti-symmetrized N-electron wave function, $1, \ldots, N$ spin and spacial coordinates of i-th electron, $i \equiv (\boldsymbol{r}_i, \sigma_i)$. Below we define functions which are called density matrices.

8.1.1 One-particle density matrix

One-particle density matrix (OPDM) is not a matrix, but a function of two arguments:

$$\rho_1(1', 1) \equiv N \int \Psi^*(1', 2, \ldots, N)\Psi(1, 2, \ldots, N) d2 \ldots dN \tag{8.1}$$

Why is it called matrix? Does not really matter... It's arguments, $1'$ and 1 which refer to coordinates of the first electron, make it look like a matrix.

Diagonal of one-particle density matrix:

$$\rho(1) \equiv \rho_1(1', 1)|_{1'=1} = N \int \Psi^*(1, 2, \ldots, N)\Psi(1, 2, \ldots, N) d2 \ldots dN \tag{8.2}$$

$\rho(1)$ is just electron density. Probability to find an electron in a volume dr is given by $\int \rho(r, \sigma) d\sigma = \rho(r)$. Normalization results: $\int \rho(1) d1 = N$.

8.1.2 Two-particle density matrix

$$\rho_2(1', 2', 1, 2) \equiv \frac{N(N-1)}{2} \int \Psi^*(1', 2', 3, \ldots, N)\Psi(1, 2, 3, \ldots, N) d3 \ldots dN \tag{8.3}$$

Diagonal of two-particle density matrix:

$$\rho_2(1,2) \equiv \rho_2(1',2',1,2)|_{1'=1,2'=2} = \frac{N(N-1)}{2}\int \Psi^*(1,2,\ldots,N)\Psi(1,2,\ldots,N)d3\ldots dN \tag{8.4}$$

8.1.3 K-particle density matrix

$$\rho_K(1',2',\ldots,K',1,2,\ldots,K) \equiv C_N^k \int \Psi^*(1',2',\ldots,K',\ldots,N)\Psi(1,2,\ldots,K,\ldots,N)dK{+}1\ldots dN \tag{8.5}$$

Relation between K and $K-1$ particle density matrix:

$$\rho_{K-1} = \frac{C_N^{K-1}}{C_N^K}\int \rho_K(1',2',\ldots,K',1,2,\ldots,K)|_{K'=K}dK \tag{8.6}$$

We always can perform integration over spin-coordinates and calculate spacial density matrix from spin density matrix.

8.1.4 Why do we need density matrices?

This is a way to compress information!

Diagonal OPDM

Diagonal OPDM defines number of electrons:

$$\int \rho(r)dr = N \tag{8.7}$$

Matrix elements of one-electron operators

For one-electron operator $A = \sum_i h_i$, where h_i is one-electron operator for i-th particle:

$$\begin{aligned} <\Psi|A|\Psi> &= \sum_{i=1}^{N} <\Psi|h_i|\Psi> = \\ \sum_{i=1}^{N}\int \Psi^*(1,2,\ldots,N)h_i\Psi(1,2,\ldots,N)d1\ldots dN &= \\ N\int \Psi^*(1,2,\ldots,N)h_1\Psi(1,2,\ldots,N)d1\ldots dN &= \\ &\int [h_1\rho_1(1',1)]_{1'=1}\,d1 \end{aligned} \tag{8.8}$$

Here we use antisymmetry of Ψ: we permute i and 1 in both Ψ^* and Ψ, and this does not change the integral. Then we can rename variables under the integral ($1 \rightarrow i$, $i \rightarrow 1$), etc.

If A does not affect spin, $<\Psi|A|\Psi> = \int [h_1\rho_1(r_1', r_1)]_{r_1'=r_1}\, dr_1$.

We have astonishing compression of information here: instead of general N-electron wave function, we have function of two coordinates only, OPDM!

Matrix elements of two-electron operators

Similarly, for any $B(1,2)$:

$$< \Psi|B|\Psi >= \int [B_{12}\rho_2(1',2',1,2)]_{1'=1,2'=2}\, d1d2 \tag{8.9}$$

For Coulomb interaction and the like ($B_{12} = B(|r_1 - r_2|)$, only diagonal part of TPDM is needed:

$$< \Psi|B|\Psi >= \int B_{12}\rho_2(r_1,r_2)dr_1dr_2 \tag{8.10}$$

Actually, we need only radial part of the dependence of ρ_2 on $r_1 - r_2$.

Energy expression

For the electronic Hamiltonian:

$$H_{el} = \sum_i T_i + \sum_i v_i + \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}} \tag{8.11}$$

total energy is given:

$$E = -\frac{1}{2}\int \nabla_r^2\rho_1(r',r)|_{r'=r}dr + \int v(r)\rho_1(r)dr + \int \frac{\rho_2(r_1,r_2)}{|r_1 - r_2|}dr_1dr_2 \tag{8.12}$$

Conclusion: to calculate energy we need only OPDM and TPDM!

Can we rewrite Shrödinger equation for density only? Not quite. We'll get set of equations up two N-particle density matrix which is equivalent to the N-electron wave function... How to truncate? Unclear.

N-representation problem: unclear, how to find only densities which correspond to antisymmetric wave function. There are developments in these directions — different approximations to truncation are used.

Matrix representation of density matrix

In practical implementations, we use matrix representations of operators and other quantities. In the basis of molecular orbitals $\{\phi_p\}$, the one-particle density matrix, $\rho_1(1',1)$, is represented as follows:

$$\rho_1(1',1) = \sum_{pq}\gamma_{pq}\phi_p(1')\phi_q(1) \tag{8.13}$$

where γ_{pq} is a matrix also called OPDM:

$$\gamma_{pq} = \int \phi_p(1')\rho_1(1',1)\phi_q(1)d1'd1 \tag{8.14}$$

$\rho_1(1',1)$ and γ_{pq} are related to the density operator described below.

Density operator and matrix of density operator

Consider operator $\hat{P}$ (also called density matrix):

$$\hat{P}\phi(1) = \int \rho_1(1',1)\phi(1')d1' = \psi(1) \tag{8.15}$$

$\hat{P}$ is one-electron operator, and ρ_1 is a kernel of integral operator $\hat{P}$. We can calculate matrix of the operator $\hat{P}$ in the basis of molecular orbitals, e.g.:

$$\gamma_{pq} = \int \phi_p(1)\rho_1(1',1)\phi_q(1')d1'd1 =< p|\hat{P}|q > \tag{8.16}$$

Can we represent density matrix operator in a second quantization? As any other one-particle operator:

$$\hat{P} = \sum_{pq} \gamma_{pq} p^+ q \tag{8.17}$$

γ_{pq} is a matrix representation of density matrix operator (in the basis of one-particle functions, e.g., spin-orbitals). γ_{pq} is also called density matrix! What is γ_{pq}, i.e., how can we calculate it? We can use Eq. (8.16), or simply calculate:

$$\gamma_{pq} =< \Psi|p^+ q|\Psi >, \tag{8.18}$$

where Ψ is N electron wave function. One can prove the above equation by combining Eq. (8.16) and Eq. (8.1):

$$\gamma_{pq} =< \phi_p|\hat{P}|\phi_q >= \int \phi_p(1')\rho_1(1',1)\phi_q(1)d1'd1 =$$
$$N\int \phi_p(1')\Psi^*(1',2,\ldots,N)\Psi(1,2,\ldots,N)\phi_q(1)d1'd1d2\ldots dN =$$
$$N\int d2\ldots dN \left(\int d1'\phi_p(1')\Psi^*(1',2,\ldots,N)\right)\left(\int d1\Psi(1,2,\ldots,N)\phi_q(1)\right) \tag{8.19}$$

What is an effect of $\int d1\Psi(1,2,\ldots,N)\phi_q(1)$? Exactly as $q|\Psi >$! Annihilation of the orbital ϕ_q from all the determinants in Ψ which contain this orbital, and annihilation of all the determinants which do not have it! Likewise, $\int d1'\phi_p(1')\Psi^*(1',2,\ldots,N) \equiv< \Psi|p^+|$.

An important property of OPDM:

$$Tr[\gamma] = N \tag{8.20}$$

Recall the number operator, $\sum_p p^+p$ and use the definition of trace to prove it. Alternatively, this can be proved by using Eq. (8.14):

$$Tr[\gamma] = \sum_p \gamma_{pp} = \int \phi_p^*(1')\rho_1(1',1)\phi_p(1)d1'd1 =$$
$$N\int \phi_p^*(1')\Psi^*(1',2,\ldots,N)\Psi(1,2,\ldots,N)\phi_q(1)d1'd1d2\ldots dN =$$
$$N\int d2\ldots dN \left(\int d1'\phi_p^*(1')\Psi^*(1',2,\ldots,N)\right)\left(\int d1\Psi(1,2,\ldots,N)\phi_p(1)\right) = N \tag{8.21}$$

H_2 example: Density Matrix for Hartree-Fock and FCI wave functions

Let us consider simple example: H_2 molecule in the minimal basis set, and let us calculate matrix of the operator $\hat{P}$ in the basis of $\sigma\alpha$, $\sigma\beta$, $\sigma^*\alpha$, and $\sigma^*\beta$ orbitals for the Hartree-Fock wave function and for the FCI wave function. We shall use second quantization to do the job. An alternative derivation is given in the next section.

We shall first calculate density matrices for the general HF wave function:

$$\gamma_{pq} =< \Phi_0|p^+q|\Phi_0 >=< \Phi_0|i^+j|\Phi_0 >= \delta_{ij} \tag{8.22}$$

Here, as usual, p, q denote general (occupied or virtual) spin-orbitals, and i, j refer to spin-orbitals occupied in Φ_0.

Thus, for the H_2 the matrix of the operator $\hat{R}$ assumes the following form in the basis of $\{\sigma\alpha, \sigma\beta, \sigma^*\alpha, \sigma^*\beta\}$ orbitals:

$$\gamma = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{8.23}$$

The result is general in a sense that for *any* Slater determinant composed of N spin-orbitals, OPDM consists of two blocks: one is diagonal unit matrix (in the occupied-occupied block), and zero for virtual-virtual block. For example, for the doubly excited determinant, $\Phi_1 = (\sigma^*)^2$, we have:

$$\gamma = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{8.24}$$

For the FCI wave function, $\Psi = C_0\Phi_0 + C_1\Phi_1$, we have:

$$\begin{aligned} \gamma_{pq} =< \Psi|p^+q|\Psi >= C_0^2 < \Phi_0|p^+q|\Phi_0 > +C_1^2 < \Phi_1|p^+q|\Phi_1 > + \\ C_0C_1 < \Phi_0|p^+q|\Phi_1 > +C_1C_0 < \Phi_1|p^+q|\Phi_0 > \end{aligned} \tag{8.25}$$

Last two terms are zero (because Φ_1 and Φ_0 do not share a single spin-orbital), thus:

$$\gamma = \begin{pmatrix} C_0^2 & 0 & 0 & 0 \\ 0 & C_0^2 & 0 & 0 \\ 0 & 0 & C_1^2 & 0 \\ 0 & 0 & 0 & C_1^2 \end{pmatrix} \tag{8.26}$$

Since $C_0^2 + C_1^2 = 1$ (normalization condition), we see that (i) eigenvalues of density matrix are non-negative and smaller or equal 1; (ii) they sum up to the number of electrons; (iii) they can be interpreted as populations of natural orbitals; and (iv) they bear some information about correlation effects in a compact form.

Alternative derivation:

For the Hartree-Fock wave function, we have:

$$\rho_1(1',1) \equiv N \int \Phi_0^*(1',2,\ldots,N)\Phi_0(1,2,\ldots,N)d2\ldots dN = \sum_{i\in\Phi_0} \phi_i^*(1')\phi_i(1) \qquad (8.27)$$

Thus, for the H_2 the matrix of the operator $\hat{R}$ assumes the following form in the basis of $\{\sigma\alpha, \sigma\beta, \sigma^*\alpha, \sigma^*\beta\}$ orbitals:

$$\gamma = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad (8.28)$$

We can see that Hartree-Fock orbitals are eigenvectors of the P, and that their eigenenergies are the same as populations of molecular orbitals in the Hartree-Fock wave function. They are greater or equal zero, and smaller or equal one. Their sum (or trace of the matrix of $\hat{R}$) is equal to the number of electrons, two in the case of H_2.

Alternatively, for the doubly excited determinant, $\Phi_1 = (\sigma^*)^2$ we have:

$$\gamma = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad (8.29)$$

For the FCI wave function, $\Psi = C_0\Phi_0 + C_1\Phi_1$, we have:

$$\begin{aligned} \rho_1(1',1) \equiv N(\int C_0^2\Phi_0^*(1',2,\ldots,N)\Phi_0(1,2,\ldots,N)d2\ldots dN + \\ \int C_1^2\Phi_1^*(1',2,\ldots,N)\Phi_1(1,2,\ldots,N)d2\ldots,dN) = \\ C_0^2(\sigma(1')\alpha(1')\sigma(1)\alpha(1) + \sigma(1')\beta(1')\sigma(1)\beta(1)) + \\ C_0^2(\sigma^*(1')\alpha(1')\sigma^*(1)\alpha(1) + \sigma^*(1')\beta(1')\sigma^*(1)\beta(1)) \end{aligned} \qquad (8.30)$$

Thus, matrix of $\hat{P}$ is:

$$\gamma = \begin{pmatrix} C_0^2 & 0 & 0 & 0 \\ 0 & C_0^2 & 0 & 0 \\ 0 & 0 & C_1^2 & 0 \\ 0 & 0 & 0 & C_1^2 \end{pmatrix} \qquad (8.31)$$

Since $C_0^2 + C_1^2 = 1$ (normalization condition), we see that (i) eigenvalues of density matrix are non-negative and smaller or equal 1; (ii) they sum up to the number of electrons; (iii) they bear some information about correlation effects in a compact form.

Natural orbitals and density matrices

We can generalize these observations. Below are listed several important properties of the density matrix operator $\hat{P}$ and corresponding density matrix γ:

1. When acts of the function from L_2, result is also L_2;

2. $\hat{P}$ is a Hermitian operator, and γ is a Hermitian matrix;

3. $\hat{P}$ has a complete set of eigenvectors $\{\phi_i\}$ with eigenvalues $\{n_i\}$. ϕ_i are called natural orbitals, n_i — populations of natural orbitals. Matrix γ is a diagonal matrix in the basis of natural orbitals.

$\int \rho_1(1)d1 = \sum_i n_i$ or $Tr[\gamma] = \sum_i n_i$;
$\rho_1(1', 1) = \sum_i n_i \phi_i^*(1')\phi_i(1) = \sum_i n_i |\phi_i >< \phi_i|$ or $P = \sum_p n_i p^+ p$;

$$\gamma = \begin{pmatrix} n_1 & 0 & \dots & 0 \\ 0 & n_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & n_i \end{pmatrix} \tag{8.32}$$

4. $0 \le n_i \le 1$. For a wave function that is a single Slater determinant all n_i equal 1 for the occupied orbitals, and zero for the virtual orbitals.

5. $\sum_i n_i = N$.

About N-representation problem:

Important property of the one-particle density is the following: If $0 \le n_i \le 1$ and $\sum_i n_i = N$, then we can write

$$\rho_1(1', 1) = \sum_k \alpha_k \rho_1^k(1', 1) \tag{8.33}$$

where $\alpha_k > 0$, $\sum_k \alpha_k = 1$ and ρ^k is OPDM for the Slater determinant composed of N natural orbitals ϕ_i.

On the other hand, any density $\rho(r)$ can represent (if $\int \rho(r)dr = N$):

$$\rho(r) = \sum_i \phi_i(r)^2 \tag{8.34}$$

Proof: Consider sphere Ω centered in the point A. Let us find such Ω that

$$\int_{\Omega_1} \rho(r)dr = 1 \tag{8.35}$$

Let us take ϕ_1 as $\sqrt{\rho}$ inside Ω and zero outside. Then can write

$$\rho(r) = \phi_1^2(r) + \rho^1(r) \tag{8.36}$$

where $\rho^1(r) \ge 0$ and $\int \rho^1(r)dr = N - 1$. Repeat N times and get $\rho(r) = \sum_i \phi_i(r)^2$. Such functions are orthonormal: $< \phi_i|\phi_j >= 0$

Two-particle density matrix

$$\Gamma_{pqrs} =< \Psi|p^+q^+sr|\Psi > \tag{8.37}$$

Density matrices and expectation values

For one-particle operators:

$$< \Psi|\hat{O}_1|\Psi >= Tr[O_1\gamma] \tag{8.38}$$

For two-particle operators:

$$< \Psi|\hat{O}_2|\Psi >= \frac{1}{2}Tr[O_2\Gamma] \tag{8.39}$$

Prove by using second quantization representation of both.

8.2 Using electronic density and density matrices for the analysis of electronic structure calculations

One-electron density characterizes electron distribution in the molecule, i.e., probability to find an electron at some point, and it is of the great quantitative and qualitative value.

Quantitative value: we need OPDM in order to calculate expectation values of one-particle density matrices, e.g., multipole moments, or spatial extent of the wave function.

Qualitative value of density is that it helps to analyze wave function in terms of familiar models of chemical bonding. Recall H_2 example: we saw that bonding orbital has more density between atomic centers than just in case of non-interacting atoms. Later on we shall discuss how to get this type of information (Bader AIM analysis).

We also would like to relate density with some familiar models:

- Lewis structures: H:O:H + two lone pairs on oxygen. Lewis structure for water would be $(core)^2(\sigma_{(OH)})^2(\sigma_{(OH)})^2(n_1)^2(n_2)^2$, where n_i denotes lone pairs on oxygen. Deviations from Lewis structures are also interesting.

- Ionicity of the bond: $\mathrm{H}^{+\delta}Cl^{-\delta}$.

- Hybridization model: sp, sp^2, sp^3, and so on.

- Bond orders, e.g., single, double, triple bonds.

Such analysis is of great interest in cases where structure of the molecule is not trivial, e.g., radicals, clusters, highly energetic species (O_4). That is why there are different schemes of wave function analysis.

8.2.1 Multipole moments

Dipole moment characterizes charge separation in the molecule. Quadrupole moments describe charge asymmetry (deviation from spherical symmetry).

The dipole moment operator is given by:

$$\boldsymbol{\mu} = -\sum_i \boldsymbol{r}_i + \sum_A Z_A \boldsymbol{R}_A \tag{8.40}$$

Expectation value of this one-electron operator is:

$$< \Psi|\mu_x|\Psi >= \int [x\rho(r', r)]|_{r=r'} dr = Tr[\mu^x \gamma] \tag{8.41}$$

where γ is a density matrix (matrix of the density operator $\hat{P}$) and μ^x is a matrix of the x-component of the dipole moment operator: $\mu^x_{pq} =< p|\mu^x|q >$.

Usually it is convenient to calculate both μ and γ in the atomic basis.

The traceless quadrupole moment tensor is defined as:

$$Q_{ij} = \sum_l q_l (3(x_i)_l \cdot (x_j)_l - r^2 \delta_{ij}), \tag{8.42}$$

where ij mark Cartesian components {XYZ} of the coordinate of the point charge q_l. For electrons, all q_l equal -1, and the electronic matrix elements of the quadrupole tensor are :

$$Q = 3 \cdot \begin{pmatrix} < \Psi|x^2 - r^2|\Psi > & < \Psi|xy|\Psi > & < \Psi|xz|\Psi > \\ < \Psi|yx|\Psi > & < \Psi|y^2 - r^2|\Psi > & < \Psi|yz|\Psi > \\ < \Psi|zx|\Psi > & < \Psi|zy|\Psi > & < \Psi|x^2 - r^2|\Psi > \end{pmatrix} \tag{8.43}$$

where $r^2 = x^2 + y^2 + z^2$. The $x^2, y^2, xy, \ldots$ operators are also one-electron operators.

The $< \Psi|x^2|\Psi >$, $< \Psi|y^2|\Psi >$, and $< \Psi|z^2|\Psi >$ matrix elements can be used to estimate the spatial extend of the wave function, e.g., in order to assign Rydberg or valence character to excited states.

8.2.2 Different orbitals

There several types of orbitals we use in electronic structure calculations:

1. Initial non-orthogonal atomic orbitals (AOs) $\{\chi_p\}$. Overlap matrix S is defined as $S_{pq} =< \chi_p|\chi_q >$.

2. Orthogonalized atomic orbitals. We can orthogonalize any given basis set in several possible ways. Since the meaning of atomic orbitals is transparent, we would like to orthogonalize AO set such that the deviation of the new set from the original one is minimal:

$$min_T ||\chi - \chi T||, \quad T^+ST = 1 \tag{8.44}$$

   where T is a transformation we seek. The result is $T = S^{-1/2}$. This is called symmetric orthogonalization, or Löwdin orthogonalization.

3. Canonical Hartree-Fock orbitals (those which diagonalize Fock operator) — delocalized molecular orbitals (MOs). They are delocalized over the entire molecule. Their energies gives IP's and EA's (Koopmans theorem).

4. Natural orbitals (NOs): those which diagonalize density operator (eigenvectors of density operator).

$$\rho(1',1) = \sum_i n_i \phi_i(1')\phi_i(1) \tag{8.45}$$

$$\hat{P} = \sum_p n_p p^+ p \tag{8.46}$$

   Natural orbitals and their population give the information about correlation. NOs are the the most compact basis for representing density.

5. Localized orbitals. Why do we need them? In order to analyze wave function. For example, we would like to write down the wave function for water in terms in localized rather than delocalized orbitals. How to define localized orbitals? There is no unique scheme. In general, variational principle is used to define localization:

$$min(<\phi_k\phi_l|g|\phi_k\phi_l>) \tag{8.47}$$

$$max(<\phi_k\phi_k|g|\phi_k\phi_k>) \tag{8.48}$$

   Or Boys localization: maximum separation of centroids???

8.2.3 Population analysis

Consider density matrix γ in the AO basis set. Number of electrons is:

$$N = \int \rho(1',1)|_{1'=1} d1 = Tr[\gamma S], \tag{8.49}$$

where γ is a density matrix in the AO basis set, and S is an overlap matrix.

Why?

$$\rho(1',1) = \sum_{\mu\nu} \gamma_{\mu\nu}\xi_\mu(1')\xi_\nu(1) \tag{8.50}$$

$$\rho(1) = \rho(1',1)|_{1'=1} = \sum_{\mu\nu} \gamma_{\mu\nu}\xi_\mu(1)\xi_\nu(1) \tag{8.51}$$

$$N = \int d1 \rho(1) = \int d1 \sum_{\mu\nu} \gamma_{\mu\nu}\xi_\mu(1)\xi_\nu(1) = \\ \sum_{\mu\nu} \gamma_{\mu\nu} \int d1 \xi_\mu(1)\xi_\nu(1) = \sum_{\mu\nu} \gamma_{\mu\nu} S_{\mu\nu} = \\ \sum_\mu (\gamma S)_{\mu\mu} = Tr[\gamma S] \tag{8.52}$$

It is possible to interpret $[\gamma S]_{\mu\mu}$ as a number of electrons associated with atomic orbital μ. This is called Mulliken population analysis:

$$q_A = Z_A - \sum_{\mu \in A} [\gamma S]_{\mu\mu} \tag{8.53}$$

where Z_A is the charge of atomic nucleus A; the index of summation indicates that we only sum over the basis functions centered on A.

This definition is by no means unique. Since $Tr[AB] = Tr[BA]$,

$$N = Tr[S^{\alpha} \gamma S^{1-\alpha}] \tag{8.54}$$

for any α. With $\alpha = \frac{1}{2}$, we have:

$$N = Tr[S^{1/2} \gamma S^{1/2}] = Tr[\gamma'], \tag{8.55}$$

where γ' is the density matrix in terms of symmetrically orthogonalized basis set. The diagonal elements of γ' are used for Löwdin population analysis:

$$q_A = Z_A - \sum_{\mu \in A} [S^{1/2} \gamma S^{1/2}]_{\mu\mu} \tag{8.56}$$

Thus, we see that both schemes involve arbitrariness. However, both can be used to observe trends, e.g., changes of bond polarity as shown in Table 8.1. Note that, though the trend (more polar bonds for more electronegative atoms) is reproduced correctly, however, absolute values are questionable. Especially dangerous would be to compare results from the different basis sets, e.g., 6-31G* calculations on methane compared to an STO-3G calculations on ammonia would predict that CH bond in the latter is more polar than the NH bond in the former. Going from the 6-31G* to 6-31G** basis set, we add more functions on hydrogen, that is why population analysis assigns more electrons to the hydrogen in ** basis set. Another example: if we would calculate H_2O in the very large basis set (up to complete basis set limit), but such that all functions are centered on oxygen, both population analysis would assign all electrons to the oxygen. Despite the ambiguity in so defined charges, this is still a useful tool of analysis.

8.2.4 Natural Bond Orbital program

The NBO program[17] is interfaced to the many electronic structure programs. Goal is to analyze electronic density in terms of Lewis structures and hybridization theory. Theory of NBO analysis is given in Ref. 18.

As input, the program uses density matrix in some basis set and these basis set orbitals. It is applicable to any wave function given that OPDM is calculated.

NBO performs series of transformations of the input basis set $\{\chi_\mu\}$ to various localized basis sets [natural atomic orbitals (NAOs), hybrid orbitals (NHOs), bond orbitals (NBOs), and localized molecular orbitals (NLMOs)]:
input basis → NAOs → NHOs → NBOs → NLMOs.

Table 8.1: Mulliken and Löwdin SCF population analysis[a]. Net charge on hydrogen is shown.

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	0.06	0.16	0.18	0.21
4-31G	0.15	0.30	0.39	0.48
6-31G*	0.16	0.33	0.43	0.52
6-31G(*,*)	0.12	0.26	0.34	0.40
STO-3G	0.03	0.10	0.13	0.15
4-31G	0.10	0.20	0.28	0.36
6-31G*	0.16	0.27	0.36	0.45
6-31G(*,*)	0.11	0.18	0.23	0.27

[a] composed table from Ref. 1.

The localized sets may be transformed to delocalized natural orbitals (NOs), or canonical molecular orbitals (MOs).

Below we discuss how these transformation are performed, and how these localized orbitals are defined. We shall also analyze Q-Chem output of NBO analysis for the water molecule.

Occupancy-weighted symmetric orthogonalization

In the NAO procedure, non-orthogonal AOs $\{\tilde{\chi}_\mu\}$ are transformed to corresponding orthonormal AOs $\{\chi_\mu\}$ by the occupancy weighted symmetric orthogonalization (OWSO) procedure:

$$\chi_\mu = \sum_\nu \tilde{\chi}_\nu T^{OWSO}_{\nu\mu} \tag{8.57}$$

The transformation matrix T^{OWSO} is found from variational principle. It minimizes the occupancy weighted mean-squared deviation of the new orbitals $\{\chi_\mu\}$ from the parent set of non-orthogonal orbitals $\{\tilde{\chi}_\mu\}$:

$$min\{\sum_\mu \omega_\mu ||\chi_\mu - \tilde{\chi}_\mu||\}, \tag{8.58}$$

where weighting factor ω_μ is taken as occupancy of $\tilde{\chi}_\mu$ (diagonal expectation value of the density operator $\hat{P}$:

$$\omega_\mu =< \tilde{\chi}_\mu|\hat{P}|\tilde{\chi}_\mu >= [\gamma S]_{\mu\mu}, \tag{8.59}$$

where γ is a density matrix in the parent basis set, and S is an overlap matrix. Such variational principle is a generalization of the Löwdin symmetric orthogonalization procedure, which corresponds to choosing $\omega_\mu = 1$ for each μ. In OWSO procedure, those orbitals having highest occupancy are most strongly preserved in their original form, while orbitals of low occupancy can distort more freely to achieve orthonormality. This procedure ensures stability in large basis sets. For small near-minimal basis sets T^{OWSO} is very close to the Löwdin transformation $S^{-1/2}$.

Natural orbitals and one-particle density matrix

Natural orbitals are defined as eigenstates of OPDM:

$$\hat{P}\phi_i = \omega_i \phi_i \tag{8.60}$$

where ω_i are called populations or occupation numbers. By their definition, NAOs have an important optimum property that leads to the most rapid convergent expansion of the electron density $\rho(r)$ in a finite basis set:

$$\rho(r) \approx \sum_{k=1}^{n} \omega_k \phi_k(r)^2 \tag{8.61}$$

Thus, NAO's are the optimal basis set to represent one-electron density.

Natural atomic orbitals

Localized NAOs are obtained as eigenvectors of localized blocks of the density matrix. Procedure is the following: diagonalize block of OPDM associated with atomic functions localized on the given atom. Then remove interatomic overlap by OWSO procedure. Orbitals centered on one atom are already orthogonal among themselves.

These orbitals are used to define NAO charges:

$$q_A = -\sum_i P_{ii}^A + Z_A \tag{8.62}$$

They also are used to define natural atomic electronic configuration, e.g., $(1s)^{1.99}(2s)^{1.90}\ldots$.

Such, inter- and intra- molecular charge transfer can be calculated. Moreover, energy change associated with this charge transfer can be calculated as well.

Bond eigenvectors: natural hybrids and natural bond orbitals

In NAOs basis, density matrix has the following form: it is diagonal in localized blocks, and it has non-diagonal non-zero blocks:

PICTURE OF P HERE

With the density matrix transformed to NAO basis, the NBO program begins search for an optimal natural Lewis structure:

1. NAOs of high occupancy (> 1.999 e) are removed as unhybridized core orbitals.

2. NAO's with an occupancy (> 1.90) are identified as lone pairs.

3. Two-centered blocks of density matrix (P^{AB}) are analyzed: program searches for bond vectors σ_{AB} (σ here is a generic notation for any occupied orbital, it can refer to π bond as well) with high occupancy (> 1.90).

4. If insufficient number of bonds is found, the program analyzes three-centered blocks and looks for three-centered bonds.

5. Each σ_{AB} is decomposed into its normalized hybrid contributions h_A and h_B from each atom:
$$\sigma_{AB} = c_A h_A + c_B h_B, \tag{8.63}$$
where h_A, h_B are so called natural hybrid orbitals composed of NAOs. Hybrids from each center participating in different bonds are symmetrically orthogonalized to remove intra-atomic overlap.

As a result, molecular wave function can be rewritten as "natural Lewis structure": $(core)^2(n_A)^2\sigma_{AB}^2$. Generally, there is some deviation from the idealized Lewis structure, e.g., not all population numbers are equal to 2. Total Lewis occupancy can be calculated and the quantity called % of Lewis structure is then can be derived. Usually, this numbers are very high: more than 99%: for ethylene, % ρ(Lewis) is 99.74%, for benzene: 97.12%. Benzene has resonance structure, which reduce the dominant character of the localized Lewis structure.

Natural localized molecular orbitals

Since total occupancy of NBOs is not equal to the number of electrons, we have some contribution of remaining weakly occupied NBOs. The most important of these are Lewis anti-bonds σ_{AB}^*:
$$\sigma_{AB}^* = c_A h_A - c_B h_B, \tag{8.64}$$

Don't get confused by these anti-bonds – they are not the same as virtual orbitals in HF theory. NBO analysis of HF wave function will produce some weakly populated natural Lewis anti-bonds. Their presence is not related to the correlation effects, but to the deviation of molecular wave function from the strictly localized Lewis structure.

Thus, these NLMOs are found by NBO program by minimizing $\sigma\sigma^*$ coupling elements of the density matrix P.

Associated energy change can be calculated.

Hyper-conjugative interactions in NBO analysis

Hyper-conjugative interactions are defined as interactions not described by Lewis structure. These are weak departures ($\sigma \rightarrow \sigma^*$) from a strictly localized Lewis structure. They are also called "non-covalent" effects.

Natural energy decomposition

Total energy can be decomposed into several components associated with a particular type of interactions.

Hartree-Fock calculations of water: NBO analysis

The current version of *Q-CHEM* supports only NBO analysis of SCF, DFT, or CC/EOM-CC wave functions. See the NBO tutorial on the web.

NBO analysis: Formaldehyde example

Geometry:

```
----------------------------------------------------
       Standard Nuclear Orientation (Angstroms)
    I     Atom         X            Y            Z
 ----------------------------------------------------
    1      C       0.000000     0.000000     0.529237
    2      O       0.000000     0.000000    -0.672963
    3      H       0.927500     0.000000     1.104138
    4      H      -0.927500     0.000000     1.104138
 ----------------------------------------------------
```

HF/6-31G(d):

```
                                     Natural Population
            Natural    -----------------------------------------------
 Atom No    Charge         Core      Valence    Rydberg      Total
 --------------------------------------------------------------------
   C  1     0.32443      1.99972     3.63992    0.03592     5.67557
   O  2    -0.58199      1.99982     6.55763    0.02454     8.58199
   H  3     0.12878      0.00000     0.86909    0.00213     0.87122
   H  4     0.12878      0.00000     0.86909    0.00213     0.87122
 ====================================================================
 * Total *  0.00000      3.99954    11.93574    0.06472    16.00000

                                 Natural Population
 --------------------------------------------------------
   Core                      3.99954 ( 99.9884% of   4)
   Valence                  11.93574 ( 99.4645% of  12)
   Natural Minimal Basis    15.93528 ( 99.5955% of  16)
   Natural Rydberg Basis     0.06472 (  0.4045% of  16)
 --------------------------------------------------------

    Atom No          Natural Electron Configuration
 ----------------------------------------------------------------------------
      C  1      [core]2s( 1.03)2p( 2.61)3s( 0.01)3p( 0.02)3d( 0.01)
      O  2      [core]2s( 1.71)2p( 4.85)3p( 0.01)3d( 0.02)
      H  3           1s( 0.87)
      H  4           1s( 0.87)
```

```
NATURAL BOND ORBITAL ANALYSIS:

                         Occupancies       Lewis Structure    Low   High
          Occ.     -------------------  -----------------   occ   occ
  Cycle   Thresh.   Lewis   Non-Lewis     CR  BD  3C  LP    (L)   (NL)   Dev
```

```
=============================================================================
  1(1)    1.90    15.89491   0.10509      2   4   0   2     0      0    0.05
-----------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

--------------------------------------------------------
  Core                      3.99954 ( 99.988% of   4)
  Valence Lewis            11.89538 ( 99.128% of  12)
 ==================       ============================
  Total Lewis              15.89491 ( 99.343% of  16)
 -------------------------------------------------------
  Valence non-Lewis         0.08099 (  0.506% of  16)
  Rydberg non-Lewis         0.02410 (  0.151% of  16)
 ==================       ============================
  Total non-Lewis           0.10509 (  0.657% of  16)
--------------------------------------------------------


    (Occupancy)   Bond orbital/ Coefficients/ Hybrids
-------------------------------------------------------------------------------
  1. (2.00000) BD ( 1) C  1- O  2
            ( 33.02%)   0.5747* C  1 s(  0.00%)p 1.00( 99.55%)d 0.00(  0.45%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.9961 -0.0570  0.0000  0.0000
                                        0.0000  0.0000 -0.0671  0.0000  0.0000
            ( 66.98%)   0.8184* O  2 s(  0.00%)p 1.00( 99.57%)d 0.00(  0.43%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.9978 -0.0062  0.0000  0.0000
                                        0.0000  0.0000  0.0658  0.0000  0.0000
  2. (1.99993) BD ( 2) C  1- O  2
            ( 33.31%)   0.5771* C  1 s( 32.17%)p 2.10( 67.51%)d 0.01(  0.32%)
                                        0.0000 -0.5626 -0.0718 -0.0052  0.0000
                                        0.0000  0.0000  0.0000  0.8163  0.0932
                                        0.0000  0.0000  0.0000  0.0082 -0.0560
            ( 66.69%)   0.8167* O  2 s( 42.56%)p 1.34( 56.92%)d 0.01(  0.52%)
                                        0.0000 -0.6519 -0.0248  0.0004  0.0000
                                        0.0000  0.0000  0.0000 -0.7543 -0.0145
                                        0.0000  0.0000  0.0000  0.0020 -0.0719
  3. (1.99573) BD ( 1) C  1- H  3
            ( 57.62%)   0.7591* C  1 s( 33.99%)p 1.94( 65.79%)d 0.01(  0.22%)
                                        0.0000  0.5827 -0.0197 -0.0013  0.7060
                                       -0.0097  0.0000  0.0000  0.3992  0.0009
                                        0.0000  0.0383  0.0000  0.0267 -0.0041
            ( 42.38%)   0.6510* H  3 s(100.00%)
```

```
                                          1.0000  0.0083
  4. (1.99573) BD ( 1) C  1- H  4
            ( 57.62%)   0.7591* C  1 s( 33.99%)p 1.94( 65.79%)d 0.01(  0.22%)
                                          0.0000  0.5827 -0.0197 -0.0013 -0.7060
                                          0.0097  0.0000  0.0000  0.3992  0.0009
                                          0.0000 -0.0383  0.0000  0.0267 -0.0041
            ( 42.38%)   0.6510* H  4 s(100.00%)
                                          1.0000  0.0083
  5. (1.99972) CR ( 1) C  1               s(100.00%)
                                          1.0000  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000  0.0000  0.0000
  6. (1.99981) CR ( 1) O  2               s(100.00%)p 0.00(  0.00%)
                                          1.0000  0.0003  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000 -0.0002  0.0000
                                          0.0000  0.0000  0.0000  0.0000  0.0000
  7. (1.98780) LP ( 1) O  2               s( 57.45%)p 0.74( 42.48%)d 0.00(  0.07%)
                                         -0.0003  0.7578 -0.0143  0.0002  0.0000
                                          0.0000  0.0000  0.0000 -0.6517 -0.0065
                                          0.0000  0.0000  0.0000  0.0021 -0.0273
  8. (1.91619) LP ( 2) O  2               s(  0.00%)p 1.00( 99.80%)d 0.00(  0.20%)
                                          0.0000  0.0000  0.0000  0.0000  0.9990
                                         -0.0077  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0443  0.0000  0.0000  0.0000
....................................
```

The shapes of natural bond orbiltals are easier to interpret that the delocalized MOs. For exmaple, the lone pair NBO is not mixed with σ_{CH}, the σ_{CH} orbitals are localized, etc.

8.2.5 Partial charges and dipole moments: Formaldehyde example

One obvious way to judge the quality of partial atomic charges $\{q_A\}$ is to compare the dipole moment computed as an expectation value for the given wave function with the dipole moment computed using partial charges derived from the same wave function:

$$\mu =< \Psi|\hat{\mu}|\Psi >= Tr[\gamma\mu] \tag{8.65}$$

$$\mu = \sum_A q_A R_A \tag{8.66}$$

If we use Å to specify the coordinates, then the the conversion factor to Debye is $1/0.52918 \cdot 2.5418 = 4.803$.

This is demonstrated for formaldehyde using HF in two different basis sets. The geometry is given above.

Results in 6-31G(d):

```
     Ground-State Mulliken Net Atomic Charges

   Atom                 Charge (a.u.)
 ----------------------------------------
     1 C                    0.134468
     2 O                   -0.427755
     3 H                    0.146644
     4 H                    0.146644
 ----------------------------------------
 Sum of atomic charges =    0.000000

 -----------------------------------------------------------------
                  Cartesian Multipole Moments
 -----------------------------------------------------------------
    Dipole Moment (Debye)
         X       0.0000      Y       0.0000      Z       2.7570
       Tot       2.7570
..........................
                                  Natural Population
              Natural    ---------------------------------------------
 Atom No      Charge        Core      Valence    Rydberg      Total
 --------------------------------------------------------------------
    C  1    0.32443      1.99972     3.63992    0.03592     5.67557
    O  2   -0.58199      1.99982     6.55763    0.02454     8.58199
    H  3    0.12878      0.00000     0.86909    0.00213     0.87122
    H  4    0.12878      0.00000     0.86909    0.00213     0.87122
 ====================================================================
 * Total *  0.00000      3.99954    11.93574    0.06472    16.00000
```

The dipole moments computed using partial Mulliken and NBO charges are 3.27 and 4.07 Debye, respectively.

Results in 6-311+G(d,p):

```
       Ground-State Mulliken Net Atomic Charges

   Atom                 Charge (a.u.)
 ----------------------------------------
     1 C                    0.106462
     2 O                   -0.308306
     3 H                    0.100922
     4 H                    0.100922
 ----------------------------------------
```

```
 Sum of atomic charges =     0.000000

 -----------------------------------------------------------------
                   Cartesian Multipole Moments
 -----------------------------------------------------------------
   Dipole Moment (Debye)
        X       0.0000      Y       0.0000      Z       2.9443
      Tot       2.9443
...............................
                                            Natural Population
               Natural    ---------------------------------------------
  Atom No    Charge         Core      Valence    Rydberg      Total
 --------------------------------------------------------------------
    C  1    0.39789      1.99971     3.56085    0.04155     5.60211
    O  2   -0.57583      1.99978     6.55715    0.01889     8.57583
    H  3    0.08897      0.00000     0.90836    0.00267     0.91103
    H  4    0.08897      0.00000     0.90836    0.00267     0.91103
 ====================================================================
 * Total *  0.00000      3.99949    11.93472    0.06579    16.00000
```

The Mulliken and NBO dipole moments are 2.34 and 3.81 Debye, respectively. Note that the trend (the dipole moment increase in a larger basis set) is not reproduced and the absolute values are quite off. However, the NBO dipoles are less basis set dependent.

Chapter 9

Practice of electronic structure calculations

9.1 Packaged programs for electronic structure calculations

There are several widely (and sometimes wildly) used *ab initio* packages which focus on different methods. Every package has a homepage, where you can find a detailed information about its functionality.

We can consider *GAUSSIAN* as a standard for basic *ab initio* calculations: SCF, DFT, MP2, QCISD, CIS methods are implemented.

Q-CHEM package is an alternative to the Gaussian. It has similar functionality, and it has very powerful tools for linear scaling. It has a variety of CC and EOM-CC codes.

GAMESS is non-commercial and it is the best MCSCF package.

Former *ACES II* (non-commercial) is the most complete coupled-cluster package. Now it is available as *ACES III* (Florida version) and *C4* (Austin-Mainz-Budapest).

PSI (non-commercial) has coupled-cluster methods, fancy CI, the best FCI code, MCSCF.

SPARTAN uses (dumbed-down) *Q-CHEM* engine and is famous for its excellent graphics and user-friendly interface.

In this course, we will use mostly *Q-CHEM*. We will begin by using *WebMO* interface, but for production-level runs on HPC we will need to learn how to manually edit input files and submit jobs using batch files.

9.2 Getting help

Up-to-date materials relevant to this course are on the web:
http://iopenshell.usc.edu/krylovgroup/chem545.html

Link "Practice of *ab initio* calculations" from this page contains some notes/links about performing and designing calculations using packaged programs. It also presents some site-specific tips, e.g., how to connect, computer usage policies, etc.

I also recommend to read some general explanations about setting up *ab initio* calculations. Check out the following links: "How to run a Quantum Chemistry Program" and "How to construct a Z-Matrix".

Q-CHEM manual can be downloaded in a PDF format. All manuals are available as hard copies in SSC#409.

9.3 How to run ab initio program?

9.3.1 Coordinates

You must specify a geometry of the molecule you you wish to study. Generally, you have two input choices:

- Cartesian: Specify the Atomic Symbol and the XYZ coordinates of the atom.
- Z-matrix: Specify the internal bond distances and angles between atoms. A ball and stick model is useful.

A simple way to perform transformation from Cartesian coordinates to intramolecular is to use *xmol* program (installed on almaak) or *jmol*.

Sources of coordinates:

1. X-ray crystallography, NMR: X-Ray is good for solid phase structures and crystallized organics and proteins. NMR is useful for liquid phase structures.
2. Books - these will provide you with bond distances between different elements. However, you will still need to determine angles on your own.
3. Previous calculations - One can use a various set of software packages to get molecular geometries.

Insight (tm) is one such useful package. You can build a molecule from fragments then optimize the geometry with a classical force field algorithm. Also, you can use the a semi-empirical method for structures such as AM1. Finally, you can use any number of *ab initio* packages to optimize a guess structure into a valid geometry.

Note that when you are performing accurate methods such as coupled-cluster theory, you should use the best geometry available, i.e., one from a SCF or MP2 geometry optimization using a medium sized basis set.

Z-matrix

A Z-matrix is used to define connectivity between atoms in a molecule. The parameters one needs are distances, angles and dihedral angles. We will show a few simple examples of how to make Z-matrices in this text. Sometimes it is a good idea to think before attempting to write a Z-matrix. What is it you are planning on doing with the molecule? If you are going to do a geometry optimization for the ground state, then it would be a good idea to enforce symmetry. Looking at the benzene example below, one can see that the D6h symmetry will never be broken. When optimizing, only the bond distances have a chance of changing, since the angles are forced to 120 degrees. However, if one is going to do a transition state search, then the Z-matrix should be as flexible as possible, to allow for any symmetry- breaking geometry changes. Taking the time to plan what one is going to do can save time hunting for why the desired output was not achieved.

Sample: Water

```
H
O 1 OH
H 2 OH 1 OHO

OH = 1.08
OHO = 107.5
```

For water, all we need is a bond distance and an angle. We start with the first atom, hydrogen, on a line of its own. The next line begins with the second atom, oxygen, and then states with which atom to measure the bond distance OH from, in this case, atom one. On the next line, the third atom, hydrogen, is OH distance away from atom two and has a bond angle of OHO in relation to atom one.

9.3.2 Charge

This determines the net charge of the system of interest and implicitly tells the program how many electrons there will be.

9.3.3 Spin Multiplicity

This field determines the net difference between up and down spins in the molecule. Note how you have to tell the program beforehand whether your molecule in the ground state is a singlet, triplet, etc. If you are not sure of the multiplicity, then run some calculations with different settings and determine which ones look reasonable. Sometimes, ground state multiplicity is self-evident. Other times, it is nearly impossible to determine the proper multiplicity because either there are near-degeneracies in the ground state, or correlation and basis set effects are crucial.

9.3.4 Basis Set

The importance of selecting a good basis set is a key to getting reasonable results. This topic will covered in more detail in the future. For now, it is important to know that the simplest basis set is a minimal one but it typically provides poor answers. Medium sized basis sets typically are 3 or 4 times larger and are useful for geometry optimizations and properties of well-behaved molecules. Finally large basis sets can be on the order of 10+ times larger than a minimal set and they are useful for "ultra-accurate" results.

9.3.5 Methods

One can choose from a multitude of methods which include:

1. SCF - Self Consistent Field theory (Ground State)
    - Hartree - Fock theory : A starting point for correlated and excited state methods;
    - DFT - Density Functional Theory: A quick and reasonably accurate method. (Well, some people call it Dirty Fast Trick... Do not tell it to anybody!)
2. MP2 - Moller - Plesset perturbation theory (Ground State). This is the simplest correlation correction to the SCF energy and derivatives.
3. CCD, CCSD, CCSD(T), ... - Coupled-cluster theories. These are more advanced forms of correlation corrections which correspondingly take longer to perform.
4. CI - Configuration interaction (Grd. State and Exc. State) CIS and CIS(D) are useful first approximations to excited states of molecules. Higher order CI such as CISDTQ can be useful a correlation correction to the ground state and excited states.
5. Geometry optimizations. A molecule of interest can be optimized with respect to the electronic potential energy surface generated by SCF and MP2 calculations.
6. Properties. Different programs offer a wide range of calculated properties of molecules. They include energies, dipoles, polarizabilities, vibrational frequencies, NMR shifts, ...

These are general notes about input. However, usually you have to specify much more information to set up calculations. Also, formats of input files are very different.

9.4 Tricks of the trade

Performing calculations is not simple. You can make mistakes in preparing input (most frequent problems) and program will either crush, or give an incorrect results. Therefore you have to always analyze output file. Also, it is good to perform some benchmarks to make sure that everything is correct. When starting use of another package, it is always good to run some test problems in both packages to compare results (must be same!). When starting to work on a new problem, good test is to run minimal basis set calculations in order to see that your input is correct , to analyze valence MOs, etc.

Why outputs are so large? Extra information is given to help you to check your results or to find out why the program does not work. Always look at Z-matrix program prints as an output to make sure it looks correct. Check symmetry. For the test, nuclear repulsion energy is good, since it does not depend on basis set/model, but on geometry only. Good test for performing calculations of the same molecule with different methods, bases, packages.

Then good thing to look at are molecular orbitals, analyze their symmetries and energies. Sometimes SCF can converge to a wrong solution (since it is non-linear problem). If you get occupied orbitals with positive energy, or virtual orbitals with negative energy, or if the HOMO-LUMO gap is too small, possibly something is very wrong. However, sometimes it can be a correct answer. Which would mean that HF breaking down. Why? Recall MP2 or H2 problem.

Frequencies: negative frequencies mean two things: this is not a minima, or HF wavefunction breaks symmetry, or is very poor.

9.5 Molecular properties

Atomic charges: characterize screening — how much density resides on atoms. Multipole moments: dipoles, quadrupoles, etc. HF: Koopmans' IP (orbital energies). Electronic spatial extent — how diffuse electron cloud is. Rydberg character. Thermochemical data — can calculate heats of formation, enthalpies. etc.

9.6 How to present results

Tables arranged as follows: Experiment: last line. Total energies are given in a first column. 6 digits in total energy is a standard. Good style is to provide nuclear repulsion energy.

Chapter 10

Electron correlation

References: 5, 6.

10.1 Introduction of the correlation problem

Electron correlation energy is defined as a difference between Hartree-Fock energy in the infinite basis set and the exact energy:

$$E_{corr} = E_{exact} - E_{HF} \tag{10.1}$$

We also can define correlation energy in the given finite basis set:

$$E_{corr} = E_{FCI} - E_{HF}, \tag{10.2}$$

where E_{HF} is Hartree-Fock energy in the given finite basis set, and E_{FCI} is full configuration interaction energy calculated in the same basis set.

What is a Hartree-Fock energy? Hartree-Fock problem is finding the best single determinant wavefunction in a self-consistent field procedure, which is repeated diagonalization of an effective one-electron Hamiltonian:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} < \mu\nu||\lambda\sigma > P_{\lambda\sigma} \tag{10.3}$$

$$P_{\lambda\sigma} = \sum_{i=1}^{N} C_{\lambda i} C_{\sigma i} \tag{10.4}$$

This is a mean-field procedure. All electron interactions are averaged. Correlations are averaged out and each electron moves in the average field of the others. This means that electrons do not feel instantaneous positions of other electrons. Instead, they feel averaged in time positions of other electrons.

Our task is now to develop systematic improvements to the mean-field model.

Why correlation energy is important? On the one hand, correlation energy is usually smaller than 1% of the total electron energy. However, it is crucial because it changes in most chemical processes. Consider H_2 dissociation: at equilibrium geometry, electrons must be correlated. Their correlation energy is omitted from

Hartree-Fock wavefunction. On the dissociation limit, there is no electron correlation: each atom has one electron. Hence, for each of the individual H-atoms one electron approximation is exact. So correlation energy changes along dissociation curve from some finite value to zero. Rough order of magnitude for correlation energy is about 50-100 kJ/mol (0.5-1.0 eV) per electron pair. It is exactly the same order of magnitude as chemical transformation energies. Hence, Hartree-Fock energy for the H_2 dissociation is wrong by about 0.5-1.0 eV, which is the same order of magnitude as H-H bond energy.

Like energy itself, the correlation energy scales with the size of the molecule, it is an extensive property.

Bond energies are a leading manifestations of electron correlation, but there are presumably a lot of other (may be less crucial) effects on molecular structure.

10.1.1 Chemical consequences of electron correlation

In this section we consider qualitative chemical consequences of electron correlation.

Ionicity

The Hartree-Fock model lets electrons get slightly too close to each other (because of averaging out instantaneous repulsions). Therefore, polarity is slightly overestimated by Hartree-Fock model. For example, calculated dipole moments at HF/6-31G* are typically 20% too big.

We can demonstrate that Hartree-Fock wavefunction is too ionic by considering H_2 molecule in a minimal basis set:

$$\begin{aligned} \Phi_{RHF} = \sigma\sigma(\alpha\beta - \beta\alpha) = \\ (s_A + s_B)(s_A + s_B)(\alpha\beta - \beta\alpha) = \\ (s_A s_A + s_B s_B + s_A s_B + s_B s_A)(\alpha\beta - \beta\alpha) = \\ H_A^- H_B^+ + H_A^+ H_B^- + H_A H_B + H_A H_B \end{aligned} \tag{10.5}$$

Hartree-Fock wavefunction is a mixture of ionic and covalent pieces in a fixed proportion. This is always wrong, but it is especially bad as one approach dissociation when there should be zero probability of getting H^+ and H^-!

Bond lengths

Due to ionic character, bond lengths are generally underestimated. Correspondingly, frequencies are overestimated. As a result, molecules at Hartree-Fock level of theory are too rigid.

Correlation treatment would decrease ionicity and will lead to the bond length increase. Why? The Hartree-Fock model describes chemical bond by a formation of bonding and antibonding orbitals, bonding orbitals being occupied, antibonding orbitals completely unoccupied. Full configurational interaction wavefunction includes all possible excited determinants. Hence, “electron correlation” must be associated with antibonding orbitals becoming fractionally occupied, due to other determinants mixing with Hartree-Fock one. Hence, bond length will increase, and frequencies will decrease.

Electron-molecule scattering

In the HF approximation molecule's electron see the time averaged position of the scattering electron. In reality, the molecular electrons polarize in response to the instantaneous position of the scattering electron.

Basic point: understanding the chemistry of Hartree-Fock model leads you to a rough understanding of the role of correlation without any mathematics. It should also give you some instinct for when to trust Hartree-Fock calculations and when not to.

10.1.2 Dynamical and non-dynamical correlation

We can distinguish, in general, two different effects associated with electron correlation: dynamical and non-dynamical correlation. There is no rigorous definition of these two effects. There is no rigorous way to separate these two effects as well. We distinguish dynamical and non-dynamical correlation as two asymptotic cases.

The effect of correlation is dual. Remember uncertainty principle? Is electron a particle or a wave? We can measure electron diffraction, when electrons behave as waves. On the other hand, electrons can interact with individual molecules, and we can count individual electrons when they hit luminescent screen (on impact, electrons interact with an individual molecules). When we have electron localized in space, its momentum (and, hence, kinetic energy) is undefined. Similarly, when energy of electron is well defined, its position is undefined (they behave like a waves).

Dynamical correlation can be considered as a local interaction of two electrons, their energies undefined. Non-dynamical correlation is associated with degeneracy: interaction of two electrons (may be well separated in space) with a same energy.

Since, we did not define rigorously, how do we distinguish dynamical and nondynamical correlation:

$$E_{corr} \neq E_{nd} + E_{dyn} \tag{10.6}$$

Later I'll introduce rigorous definition of both components for which we'll have this hold:

$$E_{corr} = E_{nd} + E_{dyn} \tag{10.7}$$

Dynamical correlation

Dynamical correlation is the physical effect associated with electrons avoiding each other at short range and their fluctuations being correlated at long range. This is a mostly local (in space) effect. But it is wide in energy coordinate: there are contributions from electrons with very different energy (occupying well separated in energy orbitals). Many small contributions sum up to the large quantity.

Nondynamical correlation

Nondynamical correlation arises when two or more electronic states are nearly degenerate. The electrons fluctuate with frequencies proportional to the energy gaps between electronic states. If two or more states are nearly degenerate, we have a low frequency oscillations, hence, slow electron motions. For slow electrons mean-field would not work as good as for fast electrons. Another way to see it: kinetic energy of electrons (plus nuclear-electron interaction) against pair electron-electron interactions. For slow electrons we have decrease of one-electron part of the total Hamiltonian.

Generally, degeneracy is an indication that non-dynamical correlation is important. As a pathological example, we consider electron scattering from the molecule. For a free electron which has a continuum of energy levels degeneracy is very high. As another example, consider H_2 dissociation. On dissociation limit, bonding σ and anti-bonding σ^* orbitals become degenerate. As a result two Slater determinants $(\sigma)^2$ and $(\sigma^*)^2$ become degenerate.

So non-dynamical correlation is important in

1. electron-molecule scattering;
2. bond-dissociation;
3. anions;
4. molecules with several Lewis structures;
5. diradicals.

This effect is non-local (electrons occupying degenerate orbitals can be far apart spatially), but narrow in energy coordinate (electrons occupy degenerate states).

In terms of FCI wavefunction:

$$\Psi = C_0\Phi_0 + C_L\Phi_L \tag{10.8}$$

dynamical correlation is associated with a contributions from many excited determinants with a small coefficients C_L; non-dynamical correlation is associated with a contributions from several configurations with a large coefficients.

Consider H_2 dissociation. FCI wavefunction would be all double excitations from the reference configuration $(\sigma)^2$:

$$\Psi = C_0(\sigma)^2 + C_1(\sigma^*)^2 + \sum_i C_i(\phi_i)^2 \tag{10.9}$$

At equilibrium all coefficients C_i are small. But the gross effect can be large, when we sum contributions from many determinants. On dissociation, coefficient C_1 will become very large. As a result, contribution from a single $(\sigma^*)^2$ configuration would be large. Hence, we have dynamical correlation at equilibrium, and non-dynamical correlation at dissociation limit. Which makes sense: at small distances, local effects prevail, whereas at large separations, we have non-local effects.

Picture of MO of H_2 here.

Unrestricted Hartree-Fock wavefunction as a tool to describe non-dynamical correlation

The non-dynamical correlation is the effect of mixing in a few other determinants necessary to get a qualitatively correct wavefunction (e.g. for dissociation). This can be achieved e.g. by UHF, or, alternatively by mixing a couple of determinants together.

Qualitatively correct wavefunction for σ bond dissociation:

$$\Psi = C_0(\sigma^2) + C_1(\sigma^*)^2, \tag{10.10}$$

Unrestricted Hartree-Fock wavefunction has no restriction to be of correct symmetry. Hence, variational principle will yield at dissociation limit molecular orbitals, which are localized near individual atoms, instead of delocalized molecular orbitals σ and σ^*.

$$\begin{aligned}\Phi_0^{UHF}(r \to \infty) = |s_A \alpha s_B \beta >= \frac{1}{\sqrt{2}} \begin{pmatrix} s_A(1)\alpha(1) & s_B(1)\beta(1) \\ s_A(2)\alpha(2) & s_B(2)\beta(2) \end{pmatrix} = \\ \frac{1}{\sqrt{2}}(s_A(1)\alpha(1)s_B(2)\beta(2) - s_B(1)\beta(1)s_A(2)\alpha(2))\end{aligned} \tag{10.11}$$

Hence, UHF wavefunction can describe electron localization near individual atoms. In contrast to the RHF-wavefunction, it corresponds to the pure covalent structure. However, it has incorrect symmetry. We can show that Φ_0^{UHF} is a mixture of singlet and triplet states:

$$\begin{aligned}\Psi_{cov}^{singlet} &= (s_A s_B + s_B s_A)(\alpha\beta - \beta\alpha) = \\ (s_A \alpha s_B \beta - s_B \beta s_A \alpha) &+ (s_B \alpha s_A \beta - s_A \beta s_B \alpha) \qquad (10.12) \\ \Psi_{cov}^{triplet} &= (s_A s_B - s_B s_A)(\alpha\beta + \beta\alpha) = \\ (s_A \alpha s_B \beta - s_B \beta s_A \alpha) &+ (s_A \beta s_B \alpha - s_B \alpha s_A \beta) \qquad (10.13) \\ \Psi_0^{UHF} &= \frac{1}{\sqrt{2}}(\Psi_{cov}^{singlet} + \Psi_{cov}^{triplet}) \qquad (10.14)\end{aligned}$$

UHF-wavefunction is not an eigenstate of S^2: $< S^2 > \equiv < \Psi^{UHF}|S^2|\Psi^{UHF} >=1$ on dissociation limit. Ψ^{UHF} is spin-contaminated. $< S^2 >=0$ for singlet and 2 for triplet.

10.1.3 Conclusions

Electron correlation energy is defined as a difference between exact and uncorrelated mean-field Hartree-Fock model. Hartree-Fock, an one-electron, mean-field approximation, approximates many-electron wavefunction by a single Slater determinant. Hence, following effects are omitted in Hartree-Fock model:

1. local interaction of electrons (dynamical correlation);

2. effect of several nearly degenerate configurations (non-dynamical correlation).

H_2 example: at equilibrium, we want to include local effect of electron repulsion. At dissociation, we need non-local effects: two configuration $(\sigma)^2$ and $(\sigma^*)^2$ are degenerate, we need two determinants to describe a wavefunction on dissociation limit. Hence, we have dynamical and non-dynamical correlation effects. Consider two situations for calculation of dissociation energy: Start: calculate E_{HF} of H_2 molecule at equilibrium. Then (i) calculate E_{HF} of H_2 molecule at large distance. In this case we missed dynamical correlation at equilibrium and non-dynamical correlation at dissociation. (ii) Calculate E_{HF} of each of H atoms. Then we missed only dynamical correlation energy at equilibrium. Both are important

10.2 Structure of FCI matrix and different approaches to electron correlation

10.2.1 Intermediate normalization

It is convenient to employ so called *intermediate normalization* of the wavefunction instead of familiar normalization condition:

$$< \Psi|\Psi >= 1 \tag{10.15}$$

Intermediate normalization requires that the weight of reference determinant (usually, Hartree-Fock determinant) equals unit:

$$< \Phi_0|\Psi >= 1 \tag{10.16}$$

Thus, a general wavefunction assumes the following form:

$$\Psi^{FCI} = \Phi_0 + \sum_L C_L \Phi_L \tag{10.17}$$

With normalization condition (10.15), the energy is given by the familiar expectation value:

$$E =< \Psi|H|\Psi > \tag{10.18}$$

With intermediate normalization (10.16) the energy expression assumes the following form:

$$E =< \Phi_0|H|\Psi > \tag{10.19}$$

To show that, consider matrix element $< \Phi_0|H|\Psi >$ for the wavefunction Ψ which is an eigenfunction of H. Thus, energy calculated as (10.19) is the same as calculated by (10.18) for the exact wavefunction (but not the same for an approximate). However, for some approximate models (e.g., truncated CI) both equation give the same answer.

To proceed to different approaches for correlation energy calculation, consider FCI wavefunction and compare it against HF one. Lets think our basis is large enough to be complete.

$$\Psi^{FCI} = \Phi_0 + \sum_L C_L \Phi_L = (1 + \hat{C}_1 + \hat{C}_2 + \ldots \hat{C}_N)\Phi_0, \tag{10.20}$$

where operator $\hat{C}_M$ excites M electrons in all possible ways from reference configuration Φ_0:

$$\hat{C}_1 = \sum_{i\in occ, a\in virt} t_i^a a_a^+ a_i$$
$$\hat{C}_2 = \frac{1}{4} \sum_{ij\in occ, ab\in virt} t_{ij}^{ab} a_a^+ a_b^+ a_i a_j \tag{10.21}$$

Orbital picture here. (Occupied, virtuals, several excited determinants).

FCI solution: in the basis of all Φ_L, diagonalize matrix of the total Hamiltonian, and find its eigenvalues and eigenvectors.

How does the Hamiltonian matrix look like in the basis of excited determinants?

FCI matrix picture here.....

Several observations:

1. For intermediate normalization and for Hartree-Fock reference, we have:

   $$E =< \Phi_0|H|(1+C_1+C_2+\dots C_N)\Phi_0 >=< \Phi_0|H|\Phi_0 > + < \Phi_0|H|C_2\Phi_0 >= E_0+E_{corr}, \tag{10.22}$$

   where E_0 is Hartree-Fock energy, and correlation energy E_{corr} depends explicitly only on the amplitudes (weights) of doubly excited configurations. That does not mean, however, that we can disregard all other excitations, since they are coupled through Hamiltonian with double excitations, and therefore define coefficients of doubly excited determinants in FCI wavefunction.

2. Correlation is associated with the population antibonding orbitals.

3. We can associate different orders in excitations with pair correlations, triple correlations, etc. (E.g., for H_2 only single and double excitations are possible, hence, FCI is CISD). For HeH — only triple excitations, etc. Hence, we can hope that the weight of higher order excitations would die in a FCI wf.

4. Different determinants: a few degenerate contribute a lot (have large CI coefficients) into total energy. Or a lot of non-degenerate (with small CI coefficients) contribute totally a lot into the energy. Again, first case is non-dynamical correlation, second one — dynamical correlation.

Practical electron correlation methods. Idea — try to include effects of pair-electron correlation first, then three-particle effects, and so on.

1. MCSCF theory: no dynamical correlation. Exponential as it is FCI in a smaller subspace. For small active spaces (i.e., $\sigma - \sigma^*$ and the like), scaling is just like for the Hartree-Fock method: $N^2 - N^3$.

2. Superposition of configurations (configurational interaction)

3. Perturbation theory (MP2,MP3). MP2 (2nd order P.T.) — perturbative treatment of pair correlations. $N^4 - N^5$

4. Coupled cluster theory with singles and doubles. Self-consistent treatment of pair correlations. N^6
5. The effect of triple excitations CCSD(T) theory. Corrections for triple excitations. N^7
6. Gaussian-2 theory and chemical accuracy

10.2.2 Summary

- Correlation energy: difference between exact and uncorrelated (HF) model. HF is one-electron, mean-field approximation. Effects omitted: (1) local interaction of electrons; (2) effect of several nearly degenerate configurations. H_2 example: at equilibrium, we want to include local effect of electron repulsion. At dissociation, we need non-local effects: two configuration $(\sigma)^2$ and $(\sigma^*)^2$ are degenerate, we need two determinants to describe a wavefunction on dissociation limit. Hence, we have dynamical and non-dynamical correlation effects. Consider two situations for calculation of dissociation energy: Start: calculate E_{HF} of H_2 molecule at equilibrium. Then (i) calculate E_{HF} of H_2 molecule at large distance. In this case we missed dynamical correlation at equilibrium and non-dynamical correlation at dissociation. (ii) Calculate E_{HF} of each of H atoms. Then we missed only dynamical correlation energy at equilibrium. Both are important...

- Intermediate normalization is more convenient in electronic structure: $< \Phi_0|\Psi >= 1$ (amplitude of the reference determinant is unit). For so normalized wavefunction energy is: $E =< \Phi_0|H|\Psi >$. By analyzing FCI matrix we get: $E = E_0+ < \Phi_0|H|C_2\Phi_0 >$. Hence, correlation energy is $E_{corr} =< \Phi_0|H|C_2\Phi_0 >$.

- Different determinants in FCI wavefunction: a few degenerate contribute a lot (have large CI coefficients) into total energy. Or a lot of non-degenerate (with small CI coefficients) contribute totally a lot into the energy. Again, first case is non-dynamical correlation, second one — dynamical correlation.

10.3 Configurational interaction

Good review: 19.

First ideas about electron correlation were associated with configurational interaction. If Hartree-Fock models is so good (gets 99% of the total energy), may be inclusion of several more important determinants will make it excellent? General CI wavefunction:

$$\Psi = \sum_L C_L \Phi_L \tag{10.23}$$

Consideration (MCSCF and CI): (i) how do I select important configurations? (ii) can I include a systematically chosen set of configurations?

10.3.1 MCSCF model

Goal — to describe non-dynamical correlation (effects of a small number of quasi-degenerate configurations). How to include important configurations? If we solve Hartree-Fock problem and get Φ_0, we can consider then excited determinants and select several (using our chemical intuition) which are important for a particular case. Then we can diagonalize Hamiltonian in the basis of this configurations. This is not a good approach. Why? Because orbitals were optimized in HF procedure to give a lowest energy for a single determinant! Hence, we have unbalanced description: orbitals are best for one of the determinants, and of poor quality for another. Hence, HF (SCF) model were generalized to MCSCF model, in which both orbitals and CI coefficients are optimized variationally to give a lowest energy for the wavefunction (10.23).

Consider σ-bond dissociation in H_2 molecule (Fig. 10.1). Simplest qualitatively correct wavefunction must include 2 determinants:

$$\Psi = C_0\Psi_0 + C_1\Psi_1 \tag{10.24}$$
$$\Psi_0 = (\sigma)^2$$
$$\Psi_1 = (\sigma^*)^2$$

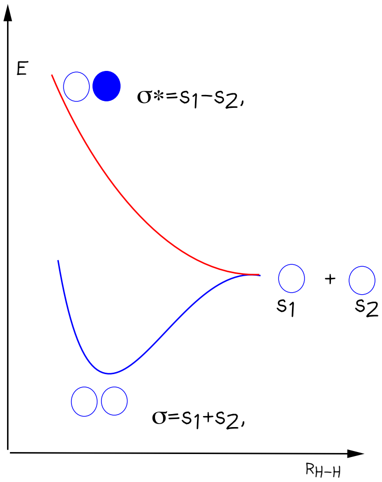


Figure 10.1: Molecular orbital picture for H_2 dissociation. At equilibrium, the two hydrogen s orbitals form bonding σ and anti-bonding σ^* orbitals which are well separated in energy. The wavefunction describing chemical bond formation can be represented by doubly occupying the σ orbital. For a large nuclear separation, when σ and σ^* are degenerate, electrons are localized near individual H atoms and occupy orbitals s_1 and s_2.

Then we optimize both orbitals and CI coefficient at each nuclear geometry. Wavefunction (10.24), often referred as a two-configuration SCF (TCSCF) wavefunction, is the simplest example of a multi-configurational SCF (MCSCF) wavefunction. In this example the orbitals σ and σ^* define the *active space* (Fig. 10.2), which is the set of orbitals whose occupations vary among the different configurations included in an MCSCF wavefunction.

If a minimal basis set is used, then the σ and σ^* orbitals are determined by symmetry, and the two configurations $(\sigma)^2$ and $(\sigma^*)^2$ are the only ones allowed by symmetry

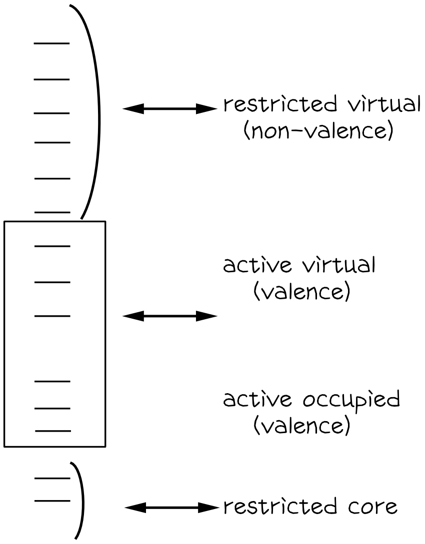


Figure 10.2: Schematic representation of active and restricted orbital spaces. Excitations are allowed within the window of active orbitals. Orbitals in each subspace are defined variationally, by minimizing total energy with respect to orbital rotations between restricted/active subspaces.

for the ground state of H_2. Hence, for this particularly simple example, the TCSCF wavefunction (10.24) happens to be identical to a full configuration interaction (FCI) wavefunction in the active space of σ and σ^* orbitals. More generally, a FCI wavefunction defined in an active space of variationally optimized orbitals is called a complete-active-space SCF (CASSCF) wavefunction,[20] also known as full optimized reaction space (FORS).[21] For the H_2 molecule, when there are only two valence orbitals, wavefunction (10.24) recovers all non-dynamical correlation.[22] For other molecules, however, the valence space contains more orbitals. Then, although two electronic configurations of the form $(\sigma)^2$ and $(\sigma^*)^2$ will dominate the dissociation of σ bonds, other electronic configurations in the valence space can be important in the zero-order wavefunction. For instance, to describe the dissociation of each particular bond in a polyatomic molecule by a TCSCF wavefunction, different σ and σ^* orbitals should be included in the active space. However, describing the dissociation of two σ bonds at the same time (or one double bond) requires an MCSCF wavefunction including four electronic configurations. More generally, a zero-order wavefunction which includes all electronic configurations that can be formed by distributing the valence electrons among the valence orbitals (bonding, anti-bonding, and lone pair orbitals) is capable of describing the breaking of any type of chemical bond (double, triple, etc.) and, moreover, the simultaneous breaking of any number of bonds. In other words, *the non-dynamical correlation energy may be defined as the difference between full configuration interaction within the space of all valence orbitals, and a single determinant of molecular orbitals (Hartree-Fock theory).*[22] Hence, the CASSCF wavefunction incorporates all non-dynamical correlation when the full valence active space is considered. Dynamical correlation energy, which is the difference between the FCI and CASSCF energies,[22] can be included later. Unfortunately, the exact calculation of non-dynamical correlation energy, as defined above, involves computational complexity that grows exponentially with molecular size and is thus unfeasible beyond systems of just two or three heavy atoms.

One strategy to approximate non-dynamical correlation for larger systems is to perform CASSCF calculations in smaller active spaces. In that case, non-dynamical correlation is no longer completely described in the zero-order wavefunction. Practically, this approximation introduces arbitrariness into theoretical descriptions because the active space is no longer uniquely defined and must be chosen based on physical considerations for each particular process. Often small active orbital spaces lead to significant errors, which cannot be completely recovered by subsequent calculations of dynamical correlation. It has been shown by Davidson[23] that CASSCF calculations for the Cope rearrangement performed in a π-orbitals active space is qualitatively incorrect, and inclusion of σ-π correlation by subsequent CASMP2 calculations changes the energetics along the reaction coordinate significantly. Another case where a large active space is necessary is reported by Chaban *et.al.*:[24] their study of N_2O_2 isomers demonstrated that the CASSCF space should include not only four NO bonds and one NN bond, but also the oxygen lone pairs. The resulting CASSCF space—14 electrons distributed in 12 orbitals, denoted (14,12)—is very close to today's limit for the CASSCF method.

Next, we consider the torsional barrier in the ethylene molecule. This example, though simple, represents a wide class of chemically important problems such as transition states and diradicals.[25,26] The molecular orbital picture of ethylene at the equilibrium geometry and along the twisting coordinate is sketched in Fig. 10.3. At the equilibrium geometry, the two carbon p orbitals perpendicular to the molecular plane form bonding π and anti-bonding π^* orbitals. The ground state (labelled the N state) doubly occupies the π-orbital. A $\pi \rightarrow \pi^*$ excitation results in the V state. Doubly occupying the π^* orbital results in the Z state. As we twist ethylene around the C–C bond, the overlap between the two p orbitals decreases and becomes zero at 90^o. Therefore, at 90^o the π and π^* orbitals become degenerate and the π bond is broken. In order to describe twisted ethylene at 90^o, we have to introduce the two configurations $(\pi)^2$ and $(\pi^*)^2$ consistently into our zero-order description.

Other examples: dissociation of double bond (C=C), or triple bond (N_2). Discuss minimal reasonable active space in each case.

Summary

MCSCF theory does not include dynamical correlation. The goal of MCSCF model is to provide correct *zero-order* wavefunction. It includes one determinant for each Lewis structure. To achieve accurate results, the dynamical correlation should be included by other models, e.g., by perturbation theory.

CASSCF wavefunction is FCI defined in an active (orbital) space with orbitals being variationally optimized. Both CI coefficients and orbitals are defined variationally.

Qualitatively correct size-consistent zero-order wavefunction suitable for PES's: CASSCF defined in a full valence space (all bonding, antibonding, and lone pairs

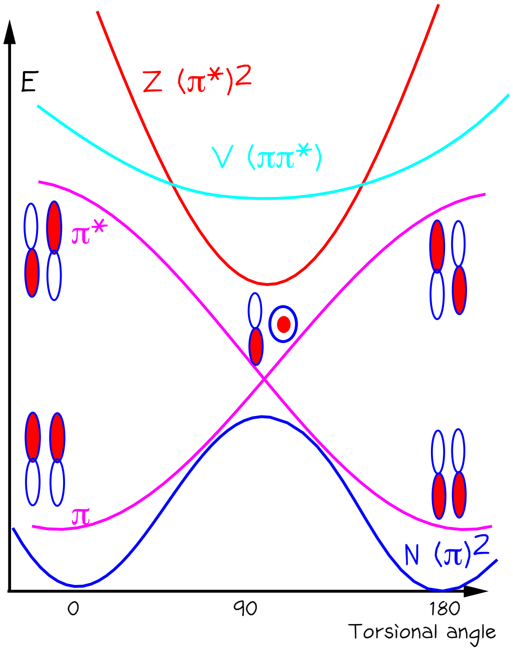


Figure 10.3: Schematic molecular orbital picture of ground and excited states of ethylene along the torsional coordinate. Twisted ethylene at 90° can be considered as a simple diradical transition state.

orbitals). It is well defined. Non-dynamical correlation energy can be defined as a correlation energy of this wavefunction. We can define then the difference between FCI and the so defined non-dynamical correlation energy. Thus:

$$E_{ex} = E_{nd} + E_{dyn} \tag{10.25}$$

Unfortunately, such calculations are unfeasible because of exponential scaling of FCI expansion. Traditional approach is to take smaller active space based on physical considerations. Criticism: MCSCF thus becomes “molecule-at-a-time”chemistry, due to the need to pick configurations (active space). It will not be systematic and could even be worse than HF if done poorly.

Tradeoff: flexibility vs. systematization. Tailored garments vs. off-the-shelf clothing!

10.3.2 Truncated CI methods

Superposition of configurations (configurational interaction) CI is a brute force approach, no chemical intuition necessary, no configuration selection should be done.

1. all double excitations? (CID)

$$\Psi_{CID} = \Phi_0 + C_2\Phi_0 = \Phi_0 + \frac{1}{4}\sum_{ijab} c_{ij}^{ab}\Phi_{ij}^{ab} \tag{10.26}$$

2. all single and double excitations? (CISD)

$$\begin{aligned} \Psi_{CISD} &= (1 + C_1 + C_2)\Phi_0 = \\ &\Phi_0 + \sum_{ia} c_i^a \Phi_i^a + \frac{1}{4} \sum_{ijab} c_{ij}^{ab} \Phi_{ij}^{ab} \end{aligned} \tag{10.27}$$

No. Or at least not acceptably. Because of the size-consistency problem. CID, CISD, MCSCF are generally not size consistent. Results degrade as molecular size increases.

E.g. CISD is exact for H_2 (same as FCI), but for 2 separate H_2, CISD is not exact, because the product wavefunction involves product of doubles (quadruples). That's why CISD (as any truncated CI method) is not size consistent. In a sense, it is worse than HF!

Reminder: Size-consistency (size-extensivity) means that calculation on a system of non-interacting fragments should give the same energy as the sum of energies from separate calculations on the individual fragments.

$$E_{AB} = E_A + E_B \tag{10.28}$$

HF is size-consistent when two closed-shell fragments are considered (for two H_2 molecules, but not for two H-atoms!) FCI is size-consistent (just like nature!) Other truncated CI methods are not. Why size-consistency is important even we do not describe bond-breaking? Because there are other manifestations, even at equilibrium geometries. For example, quality of results degrade with molecular size increase for size-inconsistent models.

We should consider theoretical model chemistries which are size-consistent! So today we do not consider truncated CI models as a practical methods for electronic correlation. However, CI provides a convenient language for correlation problem.

10.4 Many-body perturbation theory

In this section we consider perturbative treatment of electron correlation. Idea: if HF theory gets 99% of the way to the right energy, may be we can get the rest by perturbation theory. Goal of MP2 theory is to recover dynamical correlation when a zero-order wavefunction, e.g., the Hartree-Fock wavefunction, is qualitatively correct.

10.4.1 Derivation of MP2 correlation energy

Second-order perturbation theory for many-electron wavefunction was introduced by C. Møller and M.S. Plesset.[27] It is called MP2 (higher orders — MP3, MP4, etc.).

Let us recall 1-st and 2-nd orders of the Rayleigh-Schrödinger perturbation theory (with intermediate normalization of the wavefunction):

$$H_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)} \tag{10.29}$$

$$H = H_0 + \lambda V \tag{10.30}$$

$$< \Psi_i^{(0)}|\Psi_i^{(1)} >= 0 \tag{10.31}$$

$$E_i^{(1)} =< \Psi_i^{(0)}|V|\Psi_i^{(0)} > \tag{10.32}$$

$$\left(E_i^{(0)} - H_0\right)|\Psi_i^{(1)} >= \left(V - E_i^{(1)}\right)|\Psi_i^{(0)} > \tag{10.33}$$

$$E_i^{(2)} =< \Psi_i^{(0)}|V|\Psi_i^{(1)} > \tag{10.34}$$

How can we calculate PT corrections for the Hartree-Fock wavefunction? What is tricky here? To apply the RS perturbation theory we need *exact* solutions of some zero-order Hamiltonian. Can we find some Hamiltonian for which HF wavefunction is an exact solution? Yes, this is Fock operator:

$$F\Phi_K = \sum_{i\in\Phi_K} \epsilon_i \Phi_K \tag{10.35}$$

Note that the eigenenergy of $|\Phi_0>$ is not equal the Hartree-Fock energy. So, let us consider this mean-field Fock operator as our zero-order Hamiltonian. Let us consider the difference between the exact Hamiltonian and the zero-order Hamiltonian:

$$V = H - F, \tag{10.36}$$

where the perturbation V is fluctuation potential (contains electron correlations), H is the exact Hamiltonian, and F is the mean-field Fock operator of HF theory.

Imagine the matrix of H in the basis of determinants. If our starting point is HF, then the question as far as PT goes — what is it coupled to?

Matrix elements of Fock operator in the basis of determinants is very simple:

$$< \Phi_L|F|\Phi_L >= \sum_{i\in\Phi_L} \epsilon_i \tag{10.37}$$

$$< \Phi_L|F|\Phi_K >= 0, \quad K \neq L \tag{10.38}$$

So, the Fock operator is just a diagonal of the matrix. V has all non-diagonal blocks, some of them zero. Which blocks are zero? Reference – single excitations (Brillouin theorem). Also between blocks when excitation is different more than by 2. Ground state is coupled through Hamiltonian to doubles. (Slater rules, pair interaction in the exact Hamiltonian).

!! Picture here: FCI matrix and Fock matrix !!

Consider the exact problem for the ground state wavefunction:

$$H\Psi_0 = E\Psi_0 \tag{10.39}$$

Then let us expand perturbation V and wavefunction Ψ_0 in series of λ:

$$\begin{aligned}&(F + \lambda V)(\Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \ldots)\\ &= (E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \ldots)(\Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \ldots)\end{aligned} \tag{10.40}$$

Now lets collect terms proportional to the given power of λ

Zero order

Collect terms proportional to λ^0

$$\begin{aligned} F\Psi_0^{(0)} &= E_0^{(0)}\Psi_0^{(0)} \\ E_0^{(0)} &=< \Psi_0^{(0)}|F|\Psi_0^{(0)} >= \sum_i^{occ} \epsilon_i \end{aligned} \tag{10.41}$$

So, as we expected, $\Psi_0^{(0)} \equiv \Phi_0$. But $E_0^{(0)} \neq E_{HF}$!

First order

Collect terms proportional to λ^1:

$$\begin{aligned} F\Psi_0^{(1)} + V\Psi_0^{(0)} &= E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)} \\ E_0^{(1)} &=< \Psi_0^{(0)}|V|\Psi_0^{(0)} >= -\frac{1}{2}\sum_{ij}^{occ} < ij||ij > \end{aligned} \tag{10.42}$$

This is the missing part of the Hartree-Fock energy! Thus:

$$E_{HF} =< \Psi_0^{(0)}|H|\Psi_0^{(0)} >= E_0^{(0)} + E_0^{(1)} \tag{10.43}$$

the HF energy is correct through 1st order in V!

What does $\Psi_0^{(1)}$ look like?

$$(F - E_0^{(0)})\Psi_0^{(1)} = -(V - E_0^{(1)})\Psi_0^{(0)} \tag{10.44}$$

As usual $\Psi_0^{(1)}$ is orthogonal to the $\Psi_0^{(0)}$. Lets look in terms of determinants what excitations contribute to $\Psi_0^{(1)}$. We will write expression for $\Psi_0^{(1)}$ in our basis which is all excited determinants:

$$\begin{aligned} &\Psi_0^{(1)} = (T_1 + T_2 + \ldots)\Phi_0 = \\ &\sum_{ia} t_i^a \Phi_i^a + \frac{1}{2}\sum_{ijab} t_{ij}^{ab}\Phi_{ij}^{ab} + \ldots \end{aligned} \tag{10.45}$$

Now lets find coefficients t by projecting $\Psi^{(1)}$ on different determinants:

$$\begin{aligned} < \Phi_i^a|(F - E_0^{(0)})\Psi_0^{(1)} >= t_i^a(\epsilon_a - \epsilon_i) = \\ < \Phi_i^a| - (V - E^{(1)})|\Phi_0 >=< \Phi_i^a| - (H - F - E^{(1)})|\Phi_0 >= 0 \end{aligned} \tag{10.46}$$

$< \Phi_i^a|H|\Phi_0 >= 0$ by the Brillouin theorem, $< \Phi_i^a|F|\Phi_0 >= 0$ because the Fockian is just diagonal matrix in the basis of determinants, and the last term is zero due to orthonormality ($E^{(0)}$ is just a number).

Therefore, there is no single excitations in first order PT corrections to the HF wavefunction.

Double excitations

$$\begin{aligned}< \Phi_{ij}^{ab}|F - E^{(0)}|\Psi_0^{(1)} >&= (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t_{ij}^{ab} = \\ < \Phi_{ij}^{ab}| - (V - E^{(1)})|\Phi_0 >&=< \Phi_{ij}^{ab}| - (H - F)|\Phi_0 >= \\ &- < \Phi_{ij}^{ab}|H|\Phi_0 >= - < ij||ab >\end{aligned} \tag{10.47}$$

We get $< \Phi_{ij}^{ab}|H|\Phi_0 >=< ij||ab >$ by using the Slater rules. $< \Phi_{ij}^{ab}|F|\Phi_0 >$ is zero for the same reason as before: the Fockian is diagonal matrix (in the basis of excited determinants). $< \Phi_{ij}^{ab}|E^{(1)}|\Phi_0 >$ is zero because $E^{(1)}$ is just a number, and excited determinant is orthogonal to a reference one (Slater rules). Hence, the coefficients in first-order PT corrections to the wavefunction would be:

$$t_{ij}^{ab} = -\frac{< ij||ab >}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{10.48}$$

Second order

The second-order energy (MP2 energy) is:

$$\begin{aligned}F\Psi^{(2)} + V\Psi^{(1)} = E^{(0)}\Psi^{(2)} + E^{(1)}\Psi^{(1)} + E^{(2)}\Psi^{(0)} \\ E^{(2)} =< \Psi^{(0)}|V|\Psi^{(1)} >\end{aligned} \tag{10.49}$$

MP2 energy:

$$E^{(2)} = -\frac{1}{4}\sum_{ijab}\frac{< ij||ab >^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{10.50}$$

We can represent it graphically, by looking at the FCI matrix.

We should have expected this — only doubles coupled to HF determinant. Schematically,

$$\Psi^{(1)} = \sum_d t_d\Phi_d \tag{10.51}$$

$$t_d = -\frac{V_{od}}{E_d^{(0)} - E_0^{(0)}} \tag{10.52}$$

Here $\Phi_d = \Phi_{ij}^{ab}$ — doubly substituted determinants, and $t_d = t_{ij}^{ab}$ are the amplitudes (coefficients) of double substitutions.

$$E^{(2)} = \sum_d -\frac{V_{od}^2}{E_d^{(0)} - E_0^{(0)}} \tag{10.53}$$

Contributions to correlation energy from all double excitations

1. "pair correlation theory" — there is a contribution to correlation energy which comes from each pair of electrons;
2. correlation energy is negative-definite;
3. correlation energy is size-consistent;
4. the energy is not variational.

10.4.2 Computational cost of MP2 theory

$$E^{(2)} = \sum_d -\frac{V_{od}^2}{E_d^{(0)} - E_0^{(0)}} = -\frac{1}{4}\sum_{ijab} \frac{< ij||ab >^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{10.54}$$

How many doubles are there? O^2V^2. Number of occupied pairs times number of virtual pairs. Hence, there is quartic number of double excitations.

What is a cost of making the matrix elements $< ij||ab >$, two-electron integrals in the molecular orbitals basis?

Suppose we have AO integrals computed and stored. Then cost is that of transforming a 2-electron integrals from the original AO basis to the MO basis.

This is a sequence of matrix multiplies:

$$< ab||ij >= \sum_\mu C_{\mu a}\left[\sum_\nu C_{\nu b}\left[\sum_\lambda C_{\lambda i}\left[\sum_\sigma C_{\sigma j} < \mu\nu||\lambda\sigma >\right]\right]\right] \tag{10.55}$$

Costs $O(N^5)$ to make $O(N^4)$ transformed integrals (N is number of basis functions).

Hence, HF theory scales approximately $N^2 - N^3$, and this is iterative procedure (we recalculate Fockian at each self-consistent field) iteration.

MP2 theory scales as N^5, and this is non-iterative method.

10.4.3 Local MP2

For small systems, all double excitations (O^2V^2) can contribute into the total energy from Eq. (10.50). For a large system, however, number of terms which contribute into MP2 energy depend on how the orbitals are represented. The MO's that diagonalize F (canonical MO's) are delocalized. This does not change as a system gets bigger. Hence, all determinants can contribute into MP2 energy.

We can find a transformation which localizes occupied and virtual orbitals. Then we have smaller number of determinants which contribute into MP2 energy. This is a basis of local MP2 theories. Local MP2 models has been developed in MHG group bring MP2 down to quadratic (N^2) scaling by solving the equations in terms of local atomic orbital quantities.

10.4.4 Limitations of MP2 theory and higher orders of MBPT

What correlation (dynamical or non-dynamical) is MP2 capable of describing? Dynamical. The very idea of local MP2 assumes that effect is local. MP2 energy, as a HF energy depends only on the subspaces of occupied and virtual orbitals. Hence, can find transformation to local orbitals.

MP2 is a complete failure in the cases when non-dynamical correlation is important. Why? Because degeneracy disable use of perturbation theory. We can see it from Eq. (10.50), which goes to the negative infinity when orbitals become degenerate. Such, for H_2 example:

$$E_{MP2} = -\frac{< \sigma\sigma||\sigma^*\sigma^* >}{\epsilon_\sigma - \epsilon_{\sigma^*}} \tag{10.56}$$

On the dissociation limit, σ and σ^* are degenerate, hence... Other way to see it. PT assumes that perturbation V is small, and can be expanded in a small series of λ. Hence, wavefunction also can be represented as

$$\Psi = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \dots \tag{10.57}$$

However, for the cases when nondynamical correlation is important, we have several determinants in FCI expansion which have *large* expansion coefficients. For H_2 example, we have equal coefficients for both determinants at the dissociation limit. Hence, assumption that λ is a small parameter is not valid.

Collapse to the negative infinity on dissociation limit is a well-known behavior of MP2 correlation energy.

Conclusion: MP2 theory would be a complete failure for the cases when nondynamical correlation is important:

1. bond-breaking process and transition states;
2. molecules with several Lewis structures;
3. anions;
4. radicals and diradicals.

Higher orders of PT are not useful. Examples: bondlength and divergence of MP expansions. References... MP3, MP4 are occasionly used, but if MP2 has trouble the best way to fix it is not usually higher orders of PT, but rather treating electron correlation self-consistently, not perturbatively.

H_2: dissociation curve for H_2 described by MP2 would be a complete failure. However, we can achieve excellent results by doing PT on top of MCSCF wavefunction.

General consideration: include non-dynamical correlation into zero-order wavefunction. Then rest of the effects would be small, and we can make it by using PT.

10.4.5 Basis set and electron correlation methods

Why did we need basis set larger then minimal atomic basis set for HF theory? To describe how orbitals change in a molecular environment (become more diffuse, polarized in a chemical bond direction, etc). Hence, our consideration for basis set choice for HF calculations was to have basis set flexible enough to describe well occupied subspace (bonding orbitals). Something new happens as we proceed to electron correlation in general and to MP2 theory in particular. Since electron correlation is associated with antibonding and other virtual orbitals become fractionally occupied, we have represent both the virtual and occupied space accurately.

Se, we expect that there will be even more stringent requirements on the basis set than were required in HF theory!

New effects:

1. radial (in-out) correlation;

2. angular correlation;

3. two-electron cusp;

Radial (in-out) correlation

When electron is near the nucleus, other will tend to stay relatively far away. Hence, we need multiple-zeta basis sets. The "correlation-consistent" basis set of Dunning et. al.[28]

!!Figure here!!!

!! table here !!

Angular correlation

If we imagine subdividing an atom volume by angle, then there will be a tendency for stable configuration to involve electron that are in distinct angular segments. Describing this type of correlation requires higher angular momentum functions.

!! figure here!!

Two electron cusp

Similarly to electron-nuclear cusp, there is a electron-electron cusp due to Coloumb interaction of two electrons. To describe it, we need large basis sets, since it is difficult to approximate this two electron function by products of one-electron functions. This is one of the reasons for slower basis set convergence for correlated methods.

Conclusions

The *smallest* basis set suitable for use with correlation methods — DZP or 6-31G* size.

Larger basis sets such as "correlation consistent" basis sets yield further systematic improvements: cc-pVDZ cc-pVTZ cc-pVQZ cc-pVPZ.

These bases are meant to be used with frozen core. For includig core correlation effects, one needs cc-cVXZ series.

10.4.6 Performance of MP2 theory

Given an adequate basis set, MP2 is a *systematic* improvement over HF theory (in case that HF wavefunction is qualitatively correct). MP2 gives approximately 80% of correlation energy.

General performance of MP2:

- For geometries and frequencies errors significantly reduced (by factor 2-3);

- relative energetics is usually improved, but not nearly enough.

10.5 Coupled cluster theory

Objective: a more satisfactory formulation of the Shrödinger equation than configuration interaction such that *size-extensive truncation* is possible.

In configuration interaction model wavefunction is represented as a linear superposition of Slater determinants:

$$\Psi = (1 + C_1 + C_2 + \dots C_n)\Phi_0, \tag{10.58}$$

where C_m represents all possible n-fold excitations. We have seen that this is physically inappropriate when truncated. Alternative form is to take an *exponential*:

$$\Psi = \exp(T_1 + T_2 + \dots + T_n)\Phi_0 \tag{10.59}$$

T_n operators also represent n-fold excitations. Form of T_n:

$$\begin{aligned} T_1 &= \sum_{ia} t_i^a a_a^+ a_i = \sum_{ia} t_i^a a^+ i \\ T_2 &= \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^+ a_b^+ a_i a_j = \sum_{ijab} t_{ij}^{ab} a^+ b^+ ij \end{aligned} \tag{10.60}$$

Both anzats are exact when carried to n-fold excitations. We can expand exponent to see relation between CI operators and cluster operators:

$$\begin{aligned} \exp(T_1 + T_2 + \dots + T_n) = (1) + (T_1 + T_2 + \dots + T_n) + \frac{1}{2!}(T_1 + T_2 + \dots + T_n)^2 + \\ \frac{1}{3!}(T_1 + T_2 + \dots + T_n)^3 + (.10.61) \end{aligned}$$

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= T_2 + \frac{1}{2}T_1^2 \\ C_3 &= T_3 + T_1T_2 + \frac{1}{3!}T_1^3 \\ C_4 &= T_4 + T_3T_1 + \frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{4!}T_1^4 \end{aligned} \tag{10.62}$$

Comparing the groups, we see that truncating CC at singles and doubles gives us an approximate description of all higher excitations through n-fold.

Physical meaning: for CCSD, correlation between *pairs* of electrons (T_2T_2) is included. These specific quadrupole excitations are analogous to simultaneous collision of two pairs of electrons, and contributions from these events is more significant that contributions fro the collisions of four electrons.

10.5.1 Size-extensivity

Size-extensivity is immediate: product form for non-interacting fragments:

$$\exp(A + B) = \exp(A)\exp(B) \tag{10.63}$$

provided that the operators A and B commute: $[A, B] = 0$.

10.5.2 How to solve?

How can we determine the cluster coefficients?

1. variationally? No — equations do not terminate:

$$< e^{T_1+T_2}\Phi|e^{T_1+T_2}\Phi >=< \Phi|\Phi > + < T_1\Phi|T_1\Phi > + < (T_2+\frac{1}{2}T_1^2\Phi)|(T_2+\frac{1}{2}T_1^2)\Phi > + \dots \tag{10.64}$$

2. Solve eigenvalue problem in a subspace:

$$(H-E)\Psi = 0 \tag{10.65}$$

Satisfy this equation in the space of

- the HF determinant;

$$< \Phi_0|H-E|\Psi >= 0 \tag{10.66}$$

- all single substitutions:

$$< \Phi_i^a|H-E|\Psi >= 0 \tag{10.67}$$

- all double substitutions:

$$< \Phi_{ij}^{ab}|H-E|\Psi >= 0 \tag{10.68}$$

enough equations to determine:

- energy;
- single coefficients;
- double coefficients;

The above equations are very similar to the variational CISD equations. In fact, they are identical if one takes $|\Psi >= (1+C_1+C_2)\Phi_0$ and not $|\Psi >= exp(T_1+T_2)\Phi_0$. What does this similarity mean? CISD is derived by using the variational principle:

$$< \delta\Psi|H|\Psi >= 0 \tag{10.69}$$

where $\delta\Psi$ is any allowed variation of the wavefunction. For the CISD wavefunction:

$$\delta\Psi_{CISD} \in span\{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}\}, \tag{10.70}$$

i.e., belongs to the linear subspace of the reference, single, and double excitations. For the CCSD wavefunction, $\delta\Psi$ is defined as some curvilinear subspace of the same dimensionality (e.g., sphere vs. plane in 3-D space). We can approximate this more complicated manifold by the linear part:

$$\delta\Psi_{CCSD} \approx\in span\{\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}\} \tag{10.71}$$

10.5.3 CCSD model

CCSD equations

$$
\begin{aligned}
\Psi &= e^{T_1+T_2}\Phi_0 \\
<\Phi_0|H-E|\Psi &>= 0 \\
<\Phi_i^a|H-E|\Psi &>= 0 \\
<\Phi_{ij}^{ab}|H-E|\Psi &>= 0 \qquad (10.72)
\end{aligned}
$$

How the equations terminate in this case? Quite naturally, by Slater rules:

$$
\begin{aligned}
E =< \Phi_0|H|\Phi_0 > + < \Phi_0|H|(\frac{1}{2}T_1^2 + T_2)\Phi_0 >= E_{HF} + E_{corr} \\
< \Phi_i^a|H-E|(1 + T_1 + T_2 + T_1T_2 + \frac{1}{2}T_1^2 + \frac{1}{6}T_1^3)|\Phi_0 > \\
< \Phi_{ij}^{ab}|H-E|(1 + T_1 + T_2 + T_1T_2 + \frac{1}{2}T_1^2 + \frac{1}{2}T_1^2T_2\frac{1}{6}T_1^3 + \frac{1}{24}T_1^4 + \frac{1}{2}T_2^2)|\Phi_0 > \qquad (10.73) \\
(10.74)
\end{aligned}
$$

Properties of CCSD

1. Size-extensive!
2. Exact for isolated pairs of electrons. A good sign since molecules consist of interacting pairs of electrons!
3. Non-variational.
4. Computational cost is N^6 and iterative.
5. Fails for bond-breaking: explain imbalance.

Recovery of correlation energy

CCSD at equilibrium geometries recovers $\approx 95\%$ of correlation energy. Is this enough? In general, not quite. Correlation energy is about 1 eV per local pair. This gives 4 eV correlation energy for C atom (bound to 4 neighbors). We get 0.2 eV error per C atom. This is still not quite enough — but close!

10.5.4 CCSD(T) model

What is missing in CCSD model? It is the effect of triple excitations. Let us estimate this perturbatively:

$$
< \Phi_{ijk}^{abc}|F|T_3\Phi_0 > + < \Phi_{ijk}^{abc}|V|(T_1 + T_2)\Phi_0 >= 0 \qquad (10.75)
$$

This is not PT corrections for CCSD, this is PH estimate of triples contributions. Anyway, leading contribution is due to triples.

method	scaling	iterative?
HF	N^2-N^3	yes
MP2	N^5	no (must do HF first)
CCSD	N^6	yes (must do HF first)
CCSD(T)	N^7	no (must do CCSD first)
CCSDT	N^8	yes (must do HF first)

What is its effect on the energy? Work by analogy with PT:

$$\Delta E_T = \frac{1}{36} \sum_{ijkabc} t_{ijk}^{abc} < \Phi_{ijk}^{abc} | V | T_2 \Phi_0 > \tag{10.76}$$

This method, CCSD(T), is

1. Size-extensive!
2. Computational cost is N^7 and non-iterative. CCSD must be solved first.
3. Recovers ≈ 99% of correlation energy for normal molecules. Hence can approach chemical accuracy!
4. Non-variational.

Accuracy of CCSD(T): bondlength: 0.002 Å, frequencies: ≈ 10 cm^{-1}

Alternatively, one can consider PT corrections for the CCSD wavefunctions. These will have both triples and quadruples! CCSD(2) method.

We can include effect of triples non-perturbatively, hence, we'll get CCSDT equations. How? Lets write them in class.

Lets pause to consider where we are:

Picture here: X-axis: min, DZ, DZP, 6-311G(2df) cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z. Y-axis: HF, MP2, CCSD, CCSD(T), CCSDT.

10.6 Approximation of coupled-cluster theory: quadratic CI (QCI) model

QCISD method: Ref.29.

QCI equation is an attempt to make truncated CI to be size-extensive. On the other hand, QCI equations can be viewed as an approximation to CC equations. In some cases QCI is equivalent to CC. For example, CID is the same as QCCD.

QCISD equations:

$$\begin{aligned} < \Phi_0 | H - E | \Psi >&= 0 \\ < \Phi_i^a | H - E | (1 + T_1 + T_2 + T_1 T_2) \Psi >&= 0 \\ < \Phi_{ij}^{ab} | H - E | (1 + T_1 + T_2 + \frac{1}{2} T_2^2) \Psi >&= 0 \end{aligned} \tag{10.77}$$

QCISD equations contain important non-linear terms, We can prove that the QCI energy is size-extensive (due to this terms!). Note that there is no wavefunction associated with QCI model.

Scaling of QCI is the same as scaling for CCSD, but timings are much more favorable.

10.7 Seasoned coupled cluster methods

1. Is CCSD size-extensive? Is it size-consistent? Explain.
2. Derivation of CCD equations. What is missing here? Orbital relaxation.
3. Brueckner CCD model. Optimized-orbitals CCD model. Relate to Hartree-Fock equations: $< \Phi_i^a|H|\Phi_0 >= 0$, or $\frac{\partial E_0}{\partial \theta_{ia}} = 0$. Effect of single excitations in CCSD theory, T_1 diagnostics.
4. Coupled cluster wavefunctions for multireference problem: VOOCCD model. Dissociation example. Ethylene example.

The excellent performance of the VOOCCD model for challenging multi-reference problems such as the torsion of ethylene and chemical bond breaking has been demonstrated in ref.[30] (See Figs. 10.4-10.6). Recently, Sherrill *et al.* compared the performance of the VOOCCD, CASSCF (in the full valence active space), and TCSCF (CASSCF in 2x2 active space) models for several molecules with significant diradical character, such as twisted ethylene, methylene, and ozone (Table 10.1 reproduces results for the methylene). The comparison of optimized geometries, energies, and molecular properties (e.g., dipole moments, frequencies and IR-intensities) has shown that VOOCCD does accurately approximate the CASSCF wavefunction, while the alternative TCSCF approximation gives much larger errors (nearly same as Hartree-Fock model).

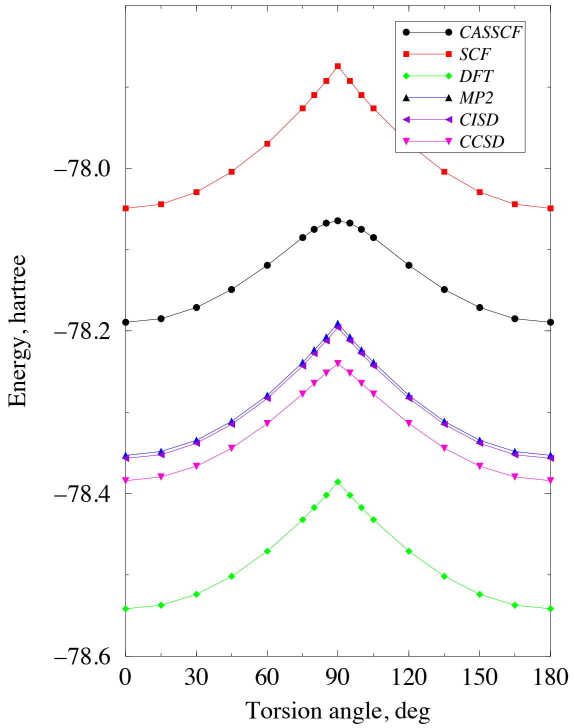


Figure 10.4: Ethylene torsional barrier using a DZP basis set. The RHF SCF energy at for the planar structure is -78.049241 hartree.

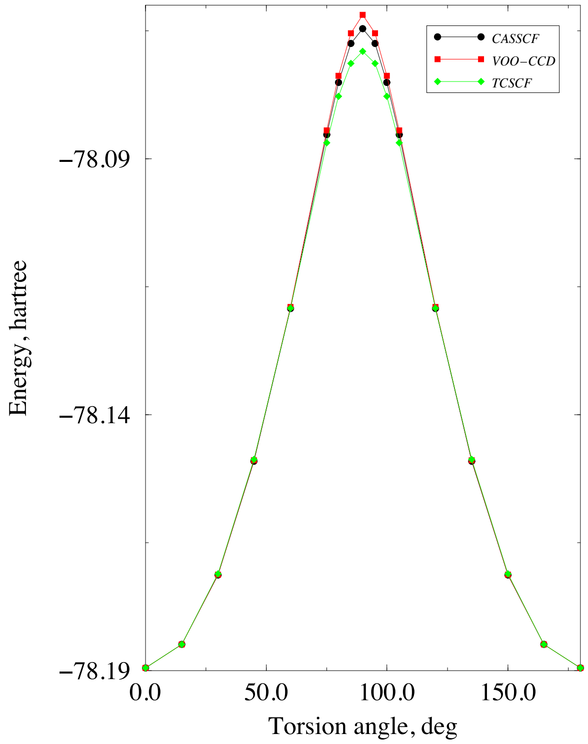


Figure 10.5: The torsional barrier for ethylene as computed by CASSCF(12,12), TCSCF [CASSCF(2,2)] and VOO-CCD using a DZP basis set. An absolute error of 0.113 hartree is subtracted from the TCSCF energy in order to compare all three curves on the same scale. The VOO-CCD total energy is -78.188456 at equilibrium and -78.061061 at the barrier.

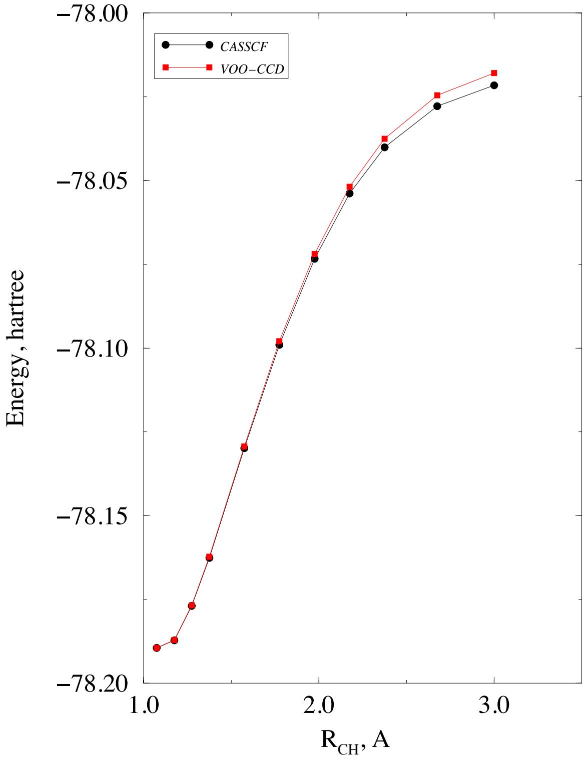


Figure 10.6: C-H bond dissociation in ethylene using CASSCF(12,12) and VOO-CCD with a DZP basis set.

Table 10.1: Comparison of the restricted Hartree-Fock, TCSCF, and VOOCCD models against CASSCF in the full valence active space. Total energies, dipole moments, equilibrium geometries, and harmonic vibrational frequencies and infrared intensities (in parentheses) are calculated for $\tilde{a}^1A_1$ CH_2 using DZP and TZ2P basis sets^a.

Method	Energy	μ_e	r_e	θ_e	ω_1 (a_1)	ω_2 (a_2)	ω_3 (a_3)
DZP RHF	-38.885 590	2.102	1.1005	103.74	3120 (61)	1490 (1)	3193 (96)
DZP TCSCF	-38.906 002	1.858	1.1035	102.72	3094 (68)	1512 (<1)	3158 (112)
DZP VOOCCD	-38.944 141	1.748	1.1333	100.65	2798 (84)	1413 (<1)	2863 (132)
DZP CASSCF	-38.944 322	1.742	1.1335	100.66	2795 (85)	1411 (<1)	2861 (133)
TZ2P RHF	-38.892 826	1.972	1.0945	103.73	3105 (64)	1503 (4)	3169 (77)
TZ2P TCSCF	-38.914 802	1.744	1.0967	102.99	3085 (67)	1527 (4)	3140 (92)
TZ2P VOOCCD	-38.953 446	1.657	1.1235	101.00	2797 (76)	1434 (<1)	2859 (103)
TZ2P CASSCF	-38.953 635	1.651	1.1238	100.98	2800 (74)	1435 (1)	2861 (102)

^{a} Bond lengths in Å, bond angles in degrees, dipole moments in Debye, frequencies in cm^{-1}, and infrared intensities in km mol^{-1}.

Chapter 11

High accuracy quantum chemistry

11.1 Overview

Chemical accuracy: errors about 1 kcal/mol $\approx$ 0.05 eV.

Approaches:

1. Complete basis extrapolation — Taylor style. (?) $|\delta \bar{E}| \approx 0.2$ kcal/mol. Tiny systems only.
2. Alternative methods to make the extrapolation from cheaper calculations... CBS models
3. Give up on extrapolation and adopt a more explicitly empirical approach,,, G1/G2 models.
4. G3 and G3S models.

Details: CBS style extrapolation — still somewhat empirical and hard to apply, but based on rigorous 2-e results

G2, G2-MP2: somewhat complicated, but efficient.

Final comments: research issues a) unphysical scaling; b) $(L+\frac{1}{2})^{-4}$convergence

11.2 Energy additivity schemes. Gaussian-1 / Gaussian-2 / Gaussian-3 theory

Gaussian-2 (G2) theory[31] approximates a very high level calculations CCSD(T)/Infinite basis by a series of lower level calculations that use finite basis sets and lower levels of electron correlation treatment in many cases. G3 and G3S theories[32,33] are somewhat improved modifications of G2 theory.

- Step 1: optimize molecular geometry. Note that low levels of theory work quite well for this purpose, hence, can use MP2/6-31G*, which is not the full basis and highest level of correlation

- Step 2: evaluate zero point energy at nuclear geometry (recall harmonic oscillator):

  $$E_{ZPE} = \frac{1}{2} \sum_{\alpha}^{modes} \hbar\omega_{\alpha} \tag{11.1}$$

  Remember, that low-level theory was pretty good for frequencies. Hence, we use HF/6-31G* geometry and HF/6-31G* frequencies scaled by 0.893 to calculate E_{ZPE}.

- Step 3.: evaluate electronic energy at optimized geometry:

  1. basic correlation energy calculation: QCISD(T)/6-311G(d,p). (QCISD(T) is a theory which can be viewed as a simplified version of CCSD(T). It performs quite similarly.)
  2. effect of basis set extensions from 6-311G(d,p) to 6-311+G(3df,2p)

     $$\Delta_{MP2} = MP2/6311 + G(3df, 2p) - MP2/6 - 311G(d, p) \tag{11.2}$$

     We are using MP2 theory instead of full CCSD(T) (or QCISD(T)). This is because the effect of such extensions is mostly to add high-energy unoccupied orbitals whose effect can be estimated reasonably well by perturbation theory. Remember, we do this for reasons of expediency only
  3. effect of basis set extensions from 6-311+G(3df,2p) to infinity. An empirical correction for the remaining basis set deficiencies is added:

     $$\Delta_{HLC} = An_{\alpha} - Bn_{\beta} \quad (n_{\alpha} \geq n_{\beta}) \tag{11.3}$$

     Value of B is the error in the energy of the H-atom. B=0.19 mhartree

     Value of A is fitted to make mean derivation from experiment zero for 55 well established heats of formation. A=4.81 mhartree ($\equiv$ 0.13 eV per electron pair)

     This sizable correction per electron pair reinforces how hard it is to get correlation energies converged with respect to basis set.

Overall term:

$$E\left[G2(MP2)\right] = E\left[QCISD(T)/6 - 311G(d, p)\right] + \delta_{MP2} + \delta_{HLC} + \delta_{ZPE} \tag{11.4}$$

11.2.1 Chemistry using G2(MP2) model

Results for first and second row compounds. Average absolute deviation compared to the experiment. MAD — mean absolute deviation

1. Dissociation energies: MAD=1.16 kcal/mol=0.050 eV.

2. Proton affinities ($M + H^+ \rightarrow MH^+$): MAD=1.04 kcal/mol=0.045eV.

3. Ionization energies ($M \to M^+ + \bar{e}$): MAD=1.24 kcal/mol=0.054 eV
4. Electron affinities ($M + \bar{e} \to M^-$): MAD=1.29 kcal/mol=0.056 eV

Overall MAD=1.58 kcal/mol, which means uncertainty is ± 3 kcal/mol. What is a range of accessible chemistry? G2(MP2) theory can be applied up to system containing about 7 first row atoms.

11.2.2 A critique of G2(MP2) theory

1. since it is based on single-reference models, it cannot describe non-dynamical correlation. Therefore can be used only to describe molecules at equilibrium. Cannot apply to study inherently multi-reference situations, such as transition states along reaction coordinate;
2. higher level correction is empirical and cannot be fully transferable;
3. use of harmonic zero-point energies and empirically scaled HF frequencies;
4. approximations in all parts of the calculation are potentially suspect;

11.2.3 Getting better accuracy

If we still want better results then a more expensive G2 model is available. It replaces MP2 evaluation of the first basis set extension effect with MP4 evaluations of basis set extension effects in stages:

1. Diffuse:

$$\Delta E(+) = E\left[MP4/6-311+G(d,p)\right] - E\left[MP4/6-311G(d,p)\right] \tag{11.5}$$

2. Higher polarization on non-H atoms:

$$\Delta E(2df) = E\left[MP4/6-311G(2df,p)\right] - E\left[MP4/6-311G(d,p)\right] \tag{11.6}$$

3. Extra polarization functions:

$$\begin{aligned} \Delta E(3df) = {} & E\left[MP2/6-311+G(3df,2p)\right] - E\left[MP2/6-311G(2df,p)\right] \\ & - E\left[MP2/6-311+G(d,p)\right] + E\left[MP2/6-311G(d,p)\right] \end{aligned} \tag{11.7}$$

Overall effect of basis set extension:

$$\Delta = \Delta E(+) + \Delta E(2df) + \Delta E(3df) \tag{11.8}$$

Result: MAD=1.21 kcal/mol.

A small but systematic improvement. Computation time is significantly increased however.

G3 theory and G3 theory using scaled energies[32,33] G3: 1.01 kcal/mol, G3S: 0.99 kcal/mol. G3 includes spin-orbital corrections and uses larger basis sets.

11.3 Alternatives to G2 theories

11.3.1 Complete basis set (CBS) methods

Instead of using higher-level correction to move to the complete basis set limit, one can attempt to extrapolate calculations using features of the known pair correlation energy function for He.

This leads to *somewhat* less expense and potentially less empiricism.

References:.[34–36]

However, the reduction in expense for simple CBS models is accompanied by a reduction in accuracy, and the reduction is relatively small.

CBS-4: MAD= 2 kcal/mol

CBS-q: MAD= 1.7 kcal/mol

CBS-Q: MAD= 1.0 kcal/mol

Note that empirical factors remain.

Chapter 12

Density functional theory

References: Reviews: Refs. 37, 38. DFT: Ref. 39. The *Q-CHEM* manual contains a concise overview of the theory and different functionals. Excellent book: 40.

Outline:

- Return to density matrices;
- Basis of DFT: Hohenberg-Kohn theorems;
- Kohn-Sham equations;
- Approximate functionals: LDA, GGA, ADM (Hybrids);
- Performance and limitations, self-interaction errors;
- New range-separated functionals (wB97X and BNL);
- Empirical dispersion correction: '-D' methods.

12.1 Hohenberg-Kohn theorems

Exact electronic density, $\rho(r)$, of the ground state defines everything about molecule. Why? First, $\int \rho(r) = N$. Second, nuclear cusp positions define location of nuclei. Third, gradient of density at nuclei defines nuclear charges (result from cusp condition).

$$\frac{\partial}{\partial r_a}\bar{\rho}(r_a)|_{r_a=0} = -2Z_a\bar{\rho}(0), \tag{12.1}$$

where $\bar{\rho}(r_a)$ is a spherical average of $\rho(\boldsymbol{r}_a)$, a radial part of electronic density. Therefore, we know positions of nuclei, their charges and number of electrons. Hence, we can write Shrödinger equation, solve it (in principle), get exact N-electron wavefunction and exact energy. Which means that we know all about the system.

The reasoning presented above summarizes the so-called Wilson proof of DFT. Here are some recollections of Mel Levy:[41] "During the conference [1979, shortly after Hohenberg-Kohn proof was presented], I had an interesting lunch with E. Bright

Wilson. I was already aware of his unpublished density-functional type existence theorem for Coulomb systems. As known from the work of Kato, the cusps of an eigenstate density determines the positions and charges on the nuclei, and hence $v(r)$. Then, integration of the density gives T and V_{ee}. Hence, an eigenstate Coulomb ρ determines H, and thus, determines all the properties of the system. (Observe, however, that Wilson's approach does not address directly variational calculations, in part because most trial densities do not belong to Coulomb eigenstates.)

What was particularly memorable for me was Wilson's reaction to the consequences of his own beautiful proof. If I remember correctly, he expressed that he actually lost some interest in the HohenbergKohn theorem and felt less optimistic about its practical implications after feeling that his proof for Coulomb densities was essentially self-evident. I guess he was not the first to assume emotionally that the value of a theorem is necessarily proportional to its difficulty of proof. But that was a long time ago."

In the discussion below, we consider the following electronic Hamiltonian:

$$H_{el} = \sum_i T_i + \sum_i v_i + \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}}, \tag{12.2}$$

where $\hat{v} = v_i$ denotes one-particle potential operator often referred to as the "external potential". In molecular applications, $\hat{v}$ is the electrostatic field due to the nuclei. It is "external" with respect to the electrons.

12.1.1 Hohenberg-Kohn theorem I

The ground state electron density $\rho(r)$ determines the external potential $v(r)$ uniquely (to within an additive constant C):

$$\rho(r) \to v(r) \quad (unique) \tag{12.3}$$

Proof (by contradiction, *reductio ad absurdum*): Let there be two external potentials $v_1(r)$, $v_2(r)$ arising from the same $\rho(r)$. Thus there will be two Hamiltonians, H_1 and H_2 with the same (ground state) density, but different wavefunctions Ψ_1 and Ψ_2:

$$H_i\Psi_i = E_i^0\Psi_i, \quad i = 1,2 \tag{12.4}$$

We can use variational principle (VP) to make the following estimations for the ground state energies:

$$E_1^0 << \Psi_2|H_1|\Psi_2 >=< \Psi_2|H_2|\Psi_2 > + < \Psi_2|H_1 - H_2|\Psi_2 >= E_2^0 + \int \rho(r)[v_1(r) - v_2(r)]dr \tag{12.5}$$

Similarly,

$$E_2^0 << \Psi_1|H_2|\Psi_1 >=< \Psi_1|H_1|\Psi_1 > + < \Psi_1|H_2 - H_1|\Psi_1 >= E_1^0 + \int \rho(r)[v_2(r) - v_1(r)]dr \tag{12.6}$$

Combining both inequalities together, we obtain contradiction:

$$E_1^0 + E_2^0 < E_2^0 + E_1^0 \tag{12.7}$$

Hence, external potential is uniquely defined by $\rho(r)$.

We can therefore represent energy as a functional of density:

$$E[\rho] = V_{ne}[\rho] + T[\rho] + V_{ee}[\rho] = \int \rho(r)v(r)dr + T[\rho] + V_{ee}[\rho] \tag{12.8}$$

We do not know what is $T[\rho]$ and $V_{ee}[\rho]$ except for the fact that $V_{ee}[\rho]$ contains Coulomb interaction $J[\rho]$:

$$J[\rho] = \frac{1}{2}\int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 \tag{12.9}$$

12.1.2 Hohenberg-Kohn theorem II

Introduces VP for the ground state density. Any approximate density, $\tilde{\rho}$, defines some $\tilde{H}$ and, therefore, $\tilde{\Psi}$. Using regular VP:

$$< \tilde{\Psi}|H|\tilde{\Psi} >= E[\tilde{\rho}] \geq E[\rho_{exact}] \tag{12.10}$$

We have equality only when $\tilde{\rho} = \rho_{exact}$.

Hence, VP for the density:

$$\delta E[\rho] - \mu\delta\left[\int \rho(r)dr - N\right] = 0 \tag{12.11}$$

Can solve them to get density. The only catch is that we do not know is how to write the functional, $E[\rho]$!

12.2 Kohn-Sham equations

$$E[\rho] = T_s[\rho] + \int \rho(r)v(r)dr + \frac{1}{2}\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} + E_{xc}[\rho], \tag{12.12}$$

where T_s is kinetic energy of non-interacting system with density $\rho(r)$ in the appropriate $v(r)$. Here $v(r)$ is just a Coulomb potential — this is a second term in the equation. The third term is the classical Coulomb electron-electron interaction (which includes self-interaction). The last term is exchange-correlation energy, and it is *defined* by Eq. (12.12)

If E_{xc} is ignored, we obtain Hartree approximation (not Hartree-Fock!).

The Kohn-Sham equations use the fact that *any density* can be represented as:

$$\rho(r) = \sum_{i=1}^{N} \phi_i^2(r), \tag{12.13}$$

where $\phi_i^2(r)$ are some orthonormal orbitals (proof).

Is there any relations between orbital $\phi_i^2(r)$ and some real one-electron functions? In some cases. Consider non-interacting electron gas (N electrons) in some external field $v(r)$. Then wavefunction of the system is *separable* and is given by a single Slater determinant composed of one-electron functions:

$$\Phi(1, \ldots N) = |\phi_1 \ldots \phi_N >, \tag{12.14}$$

where orbitals ϕ_i are solutions of one-electron problem with the Hamiltonian:

$$H = \sum_{i=1}^{N} (-\frac{1}{2}\nabla_i^2 + v(r_i)) \tag{12.15}$$

This is an exact solution of Schrödinger equation for N non-interacting electrons in the external field. Density $\rho(r)$ for the single Slater determinant is:

$$\rho(r) = N \int \Phi^2(1, \ldots, N) d2 \ldots dN d\sigma_1 = \sum_{i=1}^{N} \phi_i^2(r) \tag{12.16}$$

Hence, in a case of non-interacting gas, orbitals ϕ_i are one-electron wavefunctions.

Kohn-Sham equations:

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc} - \epsilon_i \right) \phi_i(r) = 0 \tag{12.17}$$

Here ϕ_i are just a set of one-electron functions. They are called Kohn-Sham orbitals. v_{xc} is defined as follows:

$$v_{xc}(r) \equiv \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \tag{12.18}$$

Here $v_{xc}(r)$ depends on density $\rho(r)$ — if we change ρ, v_{xc} will change. However, we write $v_{xc}(r)$ because there is a value of v_{xc} at point r defined, and we can use it as a local potential, that is, integrate it to get total E_{xc}. v_{xc} can be described as the one-electron operator for which the expectation value of the KS Slater determinant is E_{xc}:

$$E_{xc}[\rho(r)] = \int \rho(r) v_{xc}[\rho(r)] dr \tag{12.19}$$

Kohn-Sham energy is then:

$$E = E_T + E_V + E_J + E_{XC}, \tag{12.20}$$

where each term is a functional of $\rho(r)$ and can be expressed in terms of Kohn-Sham orbitals and density as:

$$E_T = \sum_{i=1}^{N} -\frac{1}{2} < \phi_i | \nabla_i^2 | \phi_i > \tag{12.21}$$

$$E_V = -\sum_{A=1}^{M} \int \frac{Z_A \rho(r)}{|r - R_A|} dr \tag{12.22}$$

$$E_J = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \tag{12.23}$$

$$E_{XC} = \int \rho(r) v_{xc}[\rho(r)] dr = \int f(\rho, \nabla\rho, \ldots) dr \tag{12.24}$$

Here there was no approximation done. Equation (12.20) is the exact equation given that the v_{xc} is known. The equation is similar to Hartree-Fock equation. Orbitals ϕ_i are called Kohn-Sham orbitals, and they just represent a basis to write the density $\rho(r)$.

If we neglect v_{xc}, the resulting equation is Hartree approximating (non-interacting system of N particles, not anti-symmetrized). If we replace this term by an exact exchange:

$$E_{xc} = -\frac{1}{4}\int\int \frac{\rho_1(r,r')^2}{|r-r'|} dr dr' \tag{12.25}$$

which will give Hartree-Fock approximation. Then KS orbitals will be HF orbitals. KS orbitals are of great qualitative value. For example, for isolated system, i.e. $v(\infty) = 0$, highest ϵ_i controls asymptotic decay of ρ, and is negative of the exact many-body ionization potential.

KS equations are in principle exact, *if we use the exact v_{xc}*. On the other hand, when we use approximations for v_{xc}, we do not have a systematic way to improve quality of our calculations. This is different from other electronic structure models, such as CI or CC, when we can get exact results if we have enough computer power. Conclusion: unclear how to get exact results from DFT.

How do we solve Kohn-Sham equations? As HF equations, by self-consistent procedure in a basis set. Select basis set (usually, atomic basis), represent KS-orbitals as a linear combination of basis orbitals, get equations for the expansion coefficients and solve self-consistent problem: guess for orbitals/density → calculate effective Hamiltonian → diagonalization → check convergence → next step. In fact, same computer code is often used for the DFT and SCF calculations, apart from the changes in integral evaluations (i.e., grid techniques are used for the DFT integrals).

12.3 Approximations for E_{xc}

12.3.1 Local Density Approximation

For the uniform electron gas (called jellium) in the box with the density ρ which is constant, and with positive background E_b, uniformly spread charge of the same density:

$$E_{xc} = N\epsilon_{xc}(\rho) = \int \epsilon_{xc}(\rho)\rho dr, \tag{12.26}$$

where ϵ_{xc} is exchange-correlation energy per electron, N is number of electrons. ϵ_{xc} can be evaluated with a high precision – there are analytical expressions for the exchange part and numerical (quantum Mote Carlo calculations) results for the correlation. LDA generalizes this equation to:

$$E_{xc}^{LDA} \equiv \int \epsilon_{xc}[\rho(r)]\rho(r) dr, \tag{12.27}$$

where ϵ_{xc} is the exchange-correlation energy per particle of a *uniform* interacting electronic gas of density ρ (note, that ρ is constant for uniform gas). In LDA, the results for the uniform gas are modified in Eq. (12.27) where the *constant* ρ is replaced by a *function* $\rho(r)$. This assumes that actual density varies slowly (which is actually quite strange assumption when molecules are considered!). LDA is exact when length over which the density varies is much larger than the mean particle spacing.

Uniform electron gas exchange expression:

$$E_x[\rho(r)] = -\frac{9\alpha}{8}(\frac{3}{\pi})^{\frac{1}{3}} \int \rho(r)^{\frac{4}{3}} dr \tag{12.28}$$

For the uniform gas, $\alpha = 2/3$, for the so-called Slater exchange $\alpha = 1$, and for the DFT predecessor, the X_α method, α is empirically chosen to be 3/4. The Slater exchange expression is derived assuming that exchange hole can be approximated by a sphere of constant potential with the radius depending on the density.

LDA (or LDSA) functionals: VWN (Vosko, Wilk, Nusair), SVWN ('S' for 'Slater'). Vosko, Wilk, Nusair fit some functional form to the numerical results for the uniform gas, and used the uniform gas exchange functional given above. In SVWN, they use Slater exchange (same form, different α).

LDA does not have have correct asymptotic behavior. Why? because real density changes, hence, E_{xc} should be corrected by terms depending on density gradients (like Taylor expansion). KS orbitals of LDA are very close to the HF orbitals.

12.3.2 Generalized Gradient Approximation

GGA models correct LDA accounting for non-uniform density by introducing gradient of density into E_{xc}:

$$E_{xc}^{GGA} = \int f(\rho(r), \nabla\rho(r))dr = E_{xc}^{LDA}[\rho(r)] + \Delta E_{xc}[\frac{|\nabla\rho|}{\rho^{4/3}}] \tag{12.29}$$

The last term depends on the dimensionless reduced gradient of density (how fast the density changes).

E_{xc}^{GGA} depends both on density and its gradient, and can reproduce correct asymptotic behavior of $\rho(r)$. Locality versus non-locality: $\nabla\rho(r)$ is a local quantity, but it allows us to get some information about density away from where we are (think Taylor expansion). What is $f(\rho(r), \nabla\rho(r))$ then?

There are several flavors of GGA exchange. Becke (denoted by 'B') has correct asymptotic behavior of energy density and includes one empirical parameter (optimized for nobel gases). Similar exchange functionals: CAM, PW, FT97, mPW. Alternative exchange with no empirical parameters: B86, P, LG, PBE.

Correlation functionals in GGA: P86, PW91, B95. The most successful so far is Lee-Yang-Parr correlation potential (LYP). It has 4 empirical parameters and has exact cancellation of SIE in one-electron systems (more on SIE later). LYP was derived from an actual correlated wavefunction for two electron system (He atom).

A complete exchange correlation: B-LYP (Becke exchange + Lee-Yang-Parr correlation). Most commonly used GGA's: BLYP, BP86, BPW91.

Criticism: most GGAs use empirical corrections. GGA is also local model, however, real exchange/correlation are non-local. However, their is some error cancellation, exchange-correlation together are more local than each of them separately.

12.3.3 Adiabatic connection methods and hybrid functionals

One can consider a system with "tunable" electron-electron interaction. Let the parameter λ define the strength of the interactions, e.g., $\lambda = 0$ correspond to a non-interacting system, whereas $\lambda = 1$ corresponds to the fully interacting system. Then, under certain assumptions, E_{xc} for the interacting system is given by the following integral:

$$E_{xc} = \int_0^1 \Psi(\lambda) V_{xc}(\lambda) \Psi(\lambda) d\lambda, \tag{12.30}$$

where $\Psi(\lambda)$ is the exact wavefunction corresponding to λ. We know what is E_{xc} at $\lambda = 0$ — it is just Hartree-Fock exchange. Thus,

$$E_{xc} = E_x^{HF} + z(E_{ex}^{DFT} - E_x^{HF}), \tag{12.31}$$

where E_{ex}^{DFT} is the (unknown) DFT exchange-correlation functional for the fully interacting system which we are after. This allows us to justify the following expression for E_{xc}:

$$E_{xc} = (1-a)E_{xc}^{DFT} + aE_x^{HF} \tag{12.32}$$

where a is a parameter $0 < a < 1$ that controls the amount of the "Hartree-Fock exchange" (sometimes misleadingly referred to as "exact exchange") in a functional. These functionals are called 'Hybrids'. One example is H&H (half-and-half) in which the fraction of HF exchange is 50%.

This idea was taken further and three-parameter hybrids were developed (e.g., B3PW91), of which the most successful is B3LYP:

$$E^{B3LYP} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + (1-c)Ex^{LSDA} + cE_c^{LYP} \tag{12.33}$$

where a,b, and c have the same values as in B3PW91: a=0.2, b=0.72, c=0.81.

12.4 Performance of DFT theory

How the KS equations are solved? Using the same self-consistent procedure as in HF. The only difference is evaluation of v_{xc} integrals. Those are computed using numerical grids. The density of the grid, which can be controlled by the user, defines accuracy. One should use tighter grids when performing finite-difference calculations of frequencies.

Some features of KS-DFT:

- Scaling is N^3, very inexpensive. Forming "Fock" matrix is about N^2. Also can be formulated using local linear scaling formulation.

- Though potentially can be exact, unclear how to get exact solution.

- Using empirical factors. As any empirical model, breaks in some cases unexpectedly. Not an *ab initio* theory.
- Variational, but, since uses empirical corrections, is not related to the exact energy.
- Geometries, frequencies: improvement over HF. Energetics: varies (MAE for B3LYP are 3 kcal/mol on the G2 set).
- Does not describe non-dynamical correlation (since using local approximations): fails for dissociation, transition states, diradicals. For energetics errors are about 6 *kcal/mol*.
- Can be extended for excited states (via time-dependent formalism).
- Fails for weakly bound systems (van der Waals interactions, hydrogen bonding).
- Self-interaction error: H_2^+ example.
- Describes well structures, frequencies, and charge densities. Discuss tables here.
- Used for *ab initio* MD: Car-Parrinello and Born-Oppehneimer. Simultaneous dynamics of electrons and nuclei (CPMD and BOMD).

12.5 Recent developments in DFT

12.5.1 Range-separated functionals

These functionals attempt to mitigate SIE by using exact HF exchange for the long-range Coulomb interaction.[42] Functionals along these lines are known variously as "Coulomb-attenuated" functionals, "range-separated" functionals, or (our preferred designation) "long-range-corrected" (LRC) density functionals. Whatever the nomenclature, these functionals are all based upon a partition of the electron–electron Coulomb potential into long- and short-range components, using the error function (erf, see Fig. 12.1):

$$\frac{1}{r_{12}} \equiv \frac{1-\mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}} \, , \tag{12.34}$$

The first term on the right in Eq. (12.34) is singular but short-range, and decays to zero on a length scale of $\sim 1/\omega$, while the second term constitutes a non-singular, long-range background. The basic idea of LRC-DFT is to utilize the short-range component of the Coulomb operator in conjunction with standard DFT exchange (including any component of Hartree–Fock exchange, if the functional is a hybrid), while at the same time incorporating full Hartree–Fock exchange using the long-range part of the Coulomb operator. This provides a rigorously correct description of the long-range distance dependence of charge-transfer excitation energies, but aims to avoid contaminating short-range exchange–correlation effects with extra Hartree–Fock exchange.

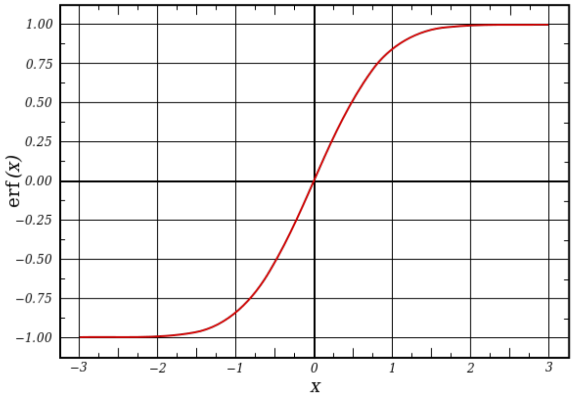


Figure 12.1: The error function (erf) is defined as: $erf(x) = \frac{2}{\pi}\int_0^x e^{-t^2}dt$. The compimentary error function, denoted by erfc, is defined as: $erfc(x) = 1 - erf(x)$.

Consider an exchange–correlation functional of the form

$$E_{\mathrm{XC}} = E_{\mathrm{C}} + E_{\mathrm{X}}^{\mathrm{GGA}} + C_{\mathrm{HF}}\, E_{\mathrm{X}}^{\mathrm{HF}}\ , \qquad (12.35)$$

in which E_{C} is the correlation energy, $E_{\mathrm{X}}^{\mathrm{GGA}}$ is the (local) GGA exchange energy, and $E_{\mathrm{X}}^{\mathrm{HF}}$ is the (non-local) Hartree–Fock exchange energy. The constant C_{HF} denotes the fraction of Hartree–Fock exchange in the functional, therefore $C_{\mathrm{HF}} = 0$ for GGAs, $C_{\mathrm{HF}} = 0.20$ for B3LYP, $C_{\mathrm{HF}} = 0.25$ for PBE0, etc. The LRC version of the generic functional in Eq. (12.35) is

$$E_{\mathrm{XC}}^{\mathrm{LRC}} = E_{\mathrm{C}} + E_{\mathrm{X}}^{\mathrm{GGA,SR}} + C_{\mathrm{HF}}\, E_{\mathrm{X}}^{\mathrm{HF,SR}} + E_{\mathrm{X}}^{\mathrm{HF,LR}}\ , \qquad (12.36)$$

in which the designations “SR” and “LR” in the various exchange energies indicate that these components of the functional are evaluated using either the short-range (SR) or the long-range (LR) component of the Coulomb operator. (The correlation energy E_{C} is evaluated using the full Coulomb operator.) The LRC functional in Eq. (12.36) incorporates full Hartree–Fock exchange in the asymptotic limit via the final term, $E_{\mathrm{X}}^{\mathrm{HF,LR}}$. To fully specify the LRC functional, one must choose a value for the range separation parameter ω in Eq. (12.34); in the limit $\omega \to 0$, the LRC functional in Eq. (12.36) reduces to the original functional in Eq. (12.35), while the $\omega \to \infty$ limit corresponds to a new functional, $E_{\mathrm{XC}} = E_{\mathrm{C}} + E_{\mathrm{X}}^{\mathrm{HF}}$. It is well known that full Hartree–Fock exchange is inappropriate for use with most contemporary GGA correlation functionals, so the latter limit is expected to perform quite poorly. Values of $\omega > 1.0$ bohr^{-1} are probably not worth considering.

There are several of these functionals in *Q-CHEM*. Our favorites are ωB97X[43] and BNL.[44,45]

12.5.2 Empirical dispersion-corrected functionals

This is a very simple trick[46] that works surprisingly well: an empirical $\frac{C_6}{R^6}$ potential terms are added to all atoms describing the dispersion interactions. Examples: B3LYP-D, BLYP-D, etc. Our favorite so far: ωB97X-D (Ref. 43).

12.5.3 DFT benchmarks

There are a lot of papers benchmarking different aspects of DFT using a variety of datasets. This review gives a reasonable overview of benchmakring studies: Rf. 47. Grimme's paper[48] is more recent, but he overlooked some of the best recent developments. This paper of Head-Gordon is very useful.[43]

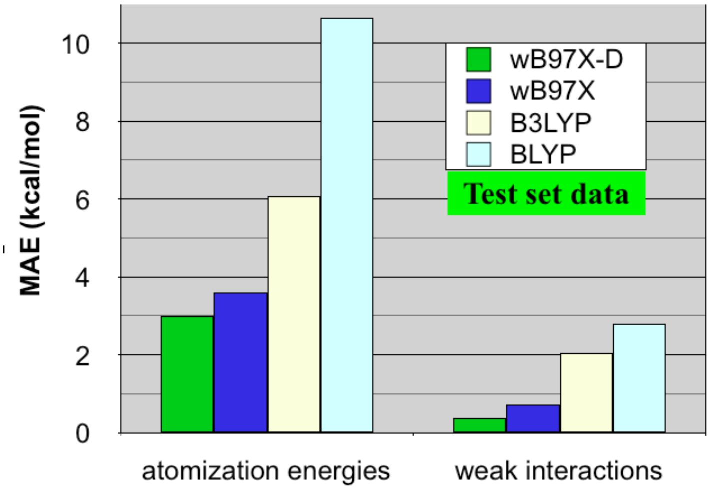


Figure 12.2: Independent comparison of an established GGA (BLYP) against an established hybrid (B3LYP), a recent range-separated hybrid (ωB97X), and a range-separated hybrid that includes an empirical long-range dispersion correction (ωB97X-D). MAE (mean average errors) are computed for the atomization energies (48 reactions comprising the G3/05 test set) and weak interactions (25 intermolecular complex binding energies).[43, 49]

Chapter 13

Excited States

13.1 What is an excited state?

What is an excited state? When a molecule absorbs a photon, it changes its energy. It can change energy of vibrations, or of the electronic state. To distinguish between different excitations, let us recall that we solve (in adiabatic approximation) the electronic Shrödinger equation:

$$H_{el}\Psi_k = E_k\Psi_k \tag{13.1}$$

The lowest eigenvalue E_0 is electronic energy of the lowest electronic state, the ground state. Higher eigenvalues correspond to excited states. We call these states electronically excited states.

How many excited states does a molecule have? Infinite number. We should distinguish between the bound (with respect to electron detachment) and continuum (above the ionization threshold) states. In this chapter, we are concerned with the low-lying electronically excited states that are below the ionization continuum.

In the two limiting cases, the excited states are simple.

If we consider the exact solution of the SE, FCI in CBS, then the lowest FCI eigenstate is our ground state, and higher FCI roots are our excited states. Ground and excited states are treated on the same footing (diagonalization of the Hamiltonian matrix).

If we consider non-interacting electrons, then any Slater determinant composed from orbitals that are eigenstates of the one-electron Hamiltonian is an eigenstate of the full Hamiltonian. The Aufbau principle tells us what is the lowest-energy state. All other electron distributions give rise to excited states, and the respective excitation energies are given by orbital differences, e.g., the excitation energy for $i \rightarrow a$ excited state is $\epsilon_a - \epsilon_i$.

What is difficult, however, is developing approximate wave functions for *interacting* electrons. The two principal problems are: (i) limitations of VP; and (ii) open-shell character of the excited-state wave functions.

13.2 Variational Principle for excited states

Recall that our approximate methods for ground-state wave functions were based on VP, e.g., the HF and KS equations were derived by applying VP, the existence of the density functional was proven via VP.

For the ground state energy, VP reads as following. For any trial wavefunction $\tilde{\Psi}$, such that $< \tilde{\Psi}|\tilde{\Psi} >= 1$

$$\tilde{E} =< \tilde{\Psi}|H|\tilde{\Psi} >\geq E_0 \tag{13.2}$$

Moreover, if the $\tilde{E} = E_0$, $\tilde{\Psi} = \Psi$. The closer $\tilde{E}$ is to E_0, the smaller is a difference (in terms of the norm) between $\tilde{\Psi}$ and Ψ.

Thus, we can say nothing about excited states energies, except for some specific cases. When the Hamiltonian matrix is block-diagonal because of symmetry (or spin symmetry), then we can apply VP in each block separately, as demonstrated for the H_2 example below.

13.3 Example: excited states of H_2 in the minimal basis

Recall H_2 problem in a minimal basis set. Molecular orbitals in a minimal basis are defined solely by symmetry:

$$\begin{aligned}\sigma &= (s_A + s_B)\\ \sigma^* &= (s_A - s_B)\end{aligned} \tag{13.3}$$

Orbital σ is gerade, σ^* — ungerade

Wavefunctions: $\sigma(1)\sigma(2)$, $\sigma^*(1)\sigma^*(2)$ are gerade; $\sigma(1)\sigma^*(2)-\sigma^*(1)\sigma(2)$, $\sigma(1)\sigma^*(2)+\sigma^*(1)\sigma(2)$ are ungerade;

Ground-state HF wavefunction:

$$|\Phi_0 >= \frac{1}{\sqrt{2}}\sigma(1)\sigma(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \tag{13.4}$$

This is singlet, gerade symmetry, Σ state: ${}^1\Sigma_g^+$. We have found from the symmetry consideration that from all excited determinants only doubly excited one is of the same symmetry and can be mixed with Ψ_0:

$$|\Phi_1 >= \frac{1}{\sqrt{2}}\sigma^*(1)\sigma^*(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \tag{13.5}$$

Solution of FCI problem in this basis will yield energies of two ${}^1\Sigma_g^+$ states. Note that determinant $|\Phi_1 >$ is not an approximation to the second ${}^1\Sigma_g^+$ state. VP only states that energy of $|\Phi_1 >$ configuration is upper bound of the ground state $|\Phi_0 >$.

Recall singly excited states. They all are of ungerade symmetry and can be both singlet and triplet. Some of the triplets are single-determinantal, whereas other are linear combination of two Slater determinants.

We have the following singly excited determinants:

- Excitation $\sigma\beta \to \sigma^*\alpha$:

$$\Phi_{\sigma\beta}^{\sigma^*\alpha} = |\sigma\alpha, \sigma^*\alpha >= \frac{1}{\sqrt{2}} \begin{pmatrix} \sigma(1)\alpha(1) & \sigma^*(1)\alpha(1) \\ \sigma(2)\alpha(2) & \sigma^*(2)\alpha(2) \end{pmatrix} = \frac{1}{\sqrt{2}} \left(\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\right) \alpha(1)\alpha(2) \tag{13.6}$$

  This is a triplet state (pure spin state)

- Similarly, excitation $\sigma\alpha \to \sigma^*\beta$:

$$\Phi_{\sigma\alpha}^{\sigma^*\beta} = |\sigma\beta, \sigma^*\beta >= \frac{1}{\sqrt{2}} \left(\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\right) \beta(1)\beta(2) \tag{13.7}$$

- Excitation $\sigma\beta \to \sigma^*\beta$

$$\Phi_{\sigma\beta}^{\sigma^*\beta} = |\sigma\alpha, \sigma^*\beta >= \frac{1}{\sqrt{2}} \begin{pmatrix} \sigma(1)\alpha(1) & \sigma^*(1)\beta(1) \\ \sigma(2)\alpha(2) & \sigma^*(2)\beta(2) \end{pmatrix} = \frac{1}{\sqrt{2}}(\sigma(1)\sigma^*(2)\alpha(1)\beta(2) - \sigma^*(1)\sigma(2)\beta(1)\alpha(2)) \tag{13.8}$$

  This is not a pure spin state (is not an eigenstate of $\hat{S}^2$).

- Similarly, excitation $\sigma\alpha \to \sigma^*\alpha$

$$\Phi_{\sigma\alpha}^{\sigma^*\alpha} = |\sigma\beta, \sigma^*\alpha >= \frac{1}{\sqrt{2}} \begin{pmatrix} \sigma(1)\beta(1) & \sigma^*(1)\alpha(1) \\ \sigma(2)\beta(2) & \sigma^*(2)\alpha(2) \end{pmatrix} = \frac{1}{\sqrt{2}}(\sigma(1)\sigma^*(2)\beta(1)\alpha(2) - \sigma^*(1)\sigma(2)\alpha(1)\beta(2)) \tag{13.9}$$

  This is not a pure spin state (is not an eigenstate of $\hat{S}^2$).

We can take linear combination of the two $M_s = 0$ determinants:

$$\frac{1}{\sqrt{2}} \left(\Phi_{\sigma\beta}^{\sigma^*\beta} + \Phi_{\sigma\alpha}^{\sigma^*\alpha}\right) = \frac{1}{2} \left(\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\right) (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \tag{13.10}$$

$$\frac{1}{2} \left(\Phi_{\sigma\beta}^{\sigma^*\beta} - \Phi_{\sigma\alpha}^{\sigma^*\alpha}\right) = \frac{1}{2} \left(\sigma(1)\sigma^*(2) + \sigma^*(1)\sigma(2)\right) (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \tag{13.11}$$

These combinations are eigen-states of $\hat{S}^2$.

The structure of FCI matrix is block-diagonal because: (i) the matrix elements between gerade and ungerade determinants are zero; and (ii) the matrix elements between different M_s determinants are zero.

One block contains two Σ_g determinants. One block has two Σ_u determinants. The high-spin Σ_u determinants form two more blocks. In each of the uncoupled blocks we can apply VP. Why? Because these states are orthogonal by symmetry (spin-symmetry) to the *exact* (FCI) lowest states of H_2.

For example, for the triplet states:

$$< \Phi_T|H|\Phi_T > \geq E(^3\Sigma_u^+) \tag{13.12}$$

However, for the singlet $^1\Sigma_u$ state, we cannot get anything useful from:

$$< \Phi_S|H|\Phi_S > \geq E(^1\Sigma_u^+) \tag{13.13}$$

because the singlet wavefunction is a combination of the two Slater determinants.

If we consider larger basis sets, the situation becomes more complicated as the sizes of different symmetry blocks increase. However, we still can find wavefunctions of the lowest triplet state by the HF procedure optimizing orbitals (which are not defined by symmetry anymore) for the high-spin determinant. This is not true for the lowest excited singlet state.

Conclusion: we cannot directly apply HF model for the excited states, except for special cases when excited state have different symmetry/spin-symmetry. Just orthogonality to an *approximate* ground-state wavefunction is not sufficient for accurate results. Even though we can apply linear VP and solve CI problem in non-interacting blocks, we cannot expect a good error cancellation for energy differences between the states (excitation energies). Moreover, we know that the error cancellation can be very poor (consider the high-spin $^3\Sigma_u$ and $X^1\Sigma_g$ states).

As follows from the analysis of the $^1\Sigma_u$ wave function, the excited states are often multi-configurational. For example, the $\mathrm{M}_s = 0$ triplet and singlet Σ_u states are linear combination of two determinants with equal weights, which is necessary to have correct spin. What are the implications of that? Consider two $M_s = 0$ determinants, $\Phi_1 = |\sigma\alpha\sigma^*\beta>$ and $\Phi_2 = |\sigma\beta\sigma^*\alpha>$. The Hamiltonian matrix in this basis is:

$$H = \begin{pmatrix} \epsilon & \Delta \\ \Delta & \epsilon \end{pmatrix}, \tag{13.14}$$

where $\epsilon =< \Phi_1|H|\Phi_1 >=< \Phi_2|H|\Phi_2 >$ and $\Delta =< \Phi_1|H|\Phi_2 >$. The eigenstates of this problem are the familiar ± combinations of the two determinants, and the respective eigenenergies are $\epsilon \pm |\Delta|$. So what is the value of Δ? Using the Slater rules to evaluate the matrix element, we obtain:

$$\Delta = - < \sigma\sigma^*|\sigma^*\sigma > \tag{13.15}$$

This is the exchange integral. For non-interacting electrons, there is no coupling (no Coulomb repulsion potential), and the spin coupling is not important, only the orbital energies matter. For the interacting electrons, the triplet and singlet states will be split by 2Δ. How large could it be? Several eV are not uncommon.

13.4 Configuration Interaction Singles

The simplest excited-state theory is CIS (Configuration Interaction Singles). The excited states are described as linear combination of singly-excited determinants, and the respective amplitudes are obtained by diagonalizing the Hamiltonian in the basis of all single excitations. Obviously, this approach can only describe the states which dominated by one-electron excitations (singly-excited states).

The formal justification of CIS relies on the Brillouin theorem, i.e., that single excitations are not coupled to the HF wavefunction. More rigorously, CIS can be derived by using linear response formalism and the Tamm-Dankoff theorem.[50, 51]

CIS yields reasonable transition energies only when HF is a good approximation for the ground-state wavefunction. We just solve the CI problem in a block of single electronic excitations. Note that we do not necessary obtain excited states energies above the ground HF state energy.

Implementations of CIS: see Refs. 52, 53.

13.4.1 Tamm-Dankoff theorem

Consider ground state HF wavefunction Φ_0. Hartree-Fock equations define set of occupied and virtual orbitals:

$$F|p>=\epsilon_p|p> \tag{13.16}$$

Consider all single excitations from $|\Phi_0>$: given by $|\Phi_i^a>$, $i\in OCC$, $a\in VIRT$. The Brillouin theorem states that $<\Phi_i^a|H|\Phi_0>=0$. which is a consequence of variational derivation of HF energy (first variation of HF wavefunction includes single excitations – only them and all of them. Variational condition says that $\delta E=<\delta\Phi_0|H|\Phi_0>=0$.

Hamiltonian projected to the subspace of HF wavefunction and single excitations is then:

$$\tilde{H}=\begin{pmatrix}\tilde{E}_{HF} & 0\\ 0 & \tilde{E}_i^a\end{pmatrix} \tag{13.17}$$

Note that VP does not imply that $\tilde{E}_k\geq\tilde{E}_{HF}$! When proving theorem for the excited states, we used re-ordered approximate states.

However, if HF is a good wavefunction, in a sense that it it much lower in energy than any of $\tilde{E}_k$, we will have than:

$$E_{HF}=\tilde{E}_0\geq E_0 \tag{13.18}$$

$$\tilde{E}_k\geq E_k \tag{13.19}$$

Than we can hope that transitions energies would be OK.

13.4.2 CIS model

This is the essence of CIS model — the eigenproblem for the Hamiltonian projected into the space of all single excitations is solved. The the resulting energies approximate excited states.

$$H^s C^s = C^s E^s \tag{13.20}$$

$$\Psi^{CIS} = \sum_{ia} C_i^a \Phi_i^a \tag{13.21}$$

Note that CIS wavefunction includes some correlation effects, since it is a linear combination of the excited determinants. It is useful to analyze the difference between CIS energies and Koopmans theorem estimates (exchange and configuration interaction).

Do we have diagnostics to predict when CIS breaks? Diagonal elements of $< \Phi_i^a|H|\Phi_j^b >$, Hamiltonian projected into the space of single excitations are equal to the sum of orbital energies from the given Slater determinant. Hence, difference between Hartree-Fock determinant and the lowest diagonal value is $E_i^a = \epsilon_a - \epsilon_i$, where i, a correspond to the HOMO and LUMO. If this gap is large, diagonalization of $\tilde{H}$ probably would not make the lowest CIS energy lower than the HF energy.

CIS calculation of water

Consider CIS calculations for water with 6-31G*. The two lowest states are:

```
Excited state   1: excitation energy (eV) =    8.7533
    Total energy for state   1:    -75.689068475536
    Multiplicity: Triplet
    Trans. Mom.:  0.0000 X   0.0000 Y   0.0000 Z
    Strength   :  0.0000
    D(  5) --> V(  1) amplitude =  0.9858

 Excited state   2: excitation energy (eV) =    9.7107
    Total energy for state   2:    -75.653883859812
    Multiplicity: Singlet
    Trans. Mom.:  0.0000 X   0.2763 Y   0.0000 Z
    Strength   :  0.0182
    D(  5) --> V(  1) amplitude =  0.9919
...................................................
 --------------------------------------------------------------
             Orbital Energies (a.u.) and Symmetries
 --------------------------------------------------------------

 Alpha MOs, Restricted
 -- Occupied --
-20.558  -1.346  -0.714  -0.571  -0.498
  1 A1    2 A1    1 B1    3 A1    1 B2
```

```
 -- Virtual --
  0.213    0.307    1.032    1.133    1.168    1.178    1.385    1.431
  4 A1     2 B1     3 B1     5 A1     2 B2     6 A1     4 B1     7 A1
  2.021    2.031    2.067    2.636    2.966    3.978
  8 A1     1 A2     3 B2     9 A1     5 B1    10 A1
```

Note the splitting between the singlet and triplet: 0.96 eV. The states have the same orbital character, HOMO→LUMO excitation. The wave functions are dominated by this transition (99%). The Koopmans estimate of the excitation energy is 0.71 hartree (19 eV)! Symmetry of these states: B_2. What is the character of these states? We need to look at the orbital shapes.

13.4.3 Excited state character.

Valence versus Rydberg excited states – see Ref. 54.

Rydberg states: What are they?

Rydberg states in atoms are defined as electronically excited states derived by exciting one of the electrons into an orbital with a principal quantum number larger than that of the valence shell.[55] Because of the diffuse character of the target orbital, these states resemble the states of a hydrogen-like atom, and their energy levels behave similarly to hydrogen-like atomic levels. This is the essence of the Rydberg formula[56] that describes the convergence of the Rydberg series in many-electron atoms to the respective ionization energies (IEs):

$$E_{ex} = IE - \frac{Ryd}{(n-\delta)^2}, \tag{13.22}$$

where E_{ex} is the excitation energy of the Rydberg state (in eV), $Ryd = 13.61$ eV, n is the principal quantum number, and δ is the quantum defect parameter accounting for the penetration of the excited Rydberg electron to the cation core.

The distinction between Rydberg and valence states in polyatomic molecules is more qualitative. Molecular Rydberg states are excited states whose configurational expansion is dominated by configurations in which the excited electron occupies diffuse (Rydberg) orbitals. Similarly to atomic Rydberg states, molecular Rydberg states can be described as having an ionized core with a weakly bound electron. Although the core is no longer spherically symmetric, the Rydberg formula can still be employed to describe energy levels. The quantum defect δ, which depends on the size and the shape of the molecule, usually has values of 0.9-1.2 for s-states, 0.3-0.9 for p-states, and smaller or equal to 0.1 for d-states.[56] These ranges are much narrower within a homologous series of molecules or radicals.[54] The situation can be more complex in molecules with closely-lying ionized states due to, for example, more than one Rydberg center. In CH_3NH_2 two Rydberg series are observed, one centered on the carbon atom and the other on the nitrogen.[57] Likewise, in vinyl radicals, one Rydberg series is obtained by exciting the unpaired electron to a Rydberg state, whereas another involves excitation of the π bond.[58]

In spite of these complications, the Rydberg formula can often be used as one of the assignment criteria of electronically excited states of molecules and radicals. For example, if the quantum defect computed by using Eq. (13.22) with known IE and E_{ex} falls within the δ interval typical of a specific class of molecules, the state with energy E_{ex} can be defined as Rydberg (provided, of course, that the character of the target MO is consistent with the suggested l, m quantum numbers). Larger deviations of δ from the characteristic values indicate interactions with nearby valence states and/or strong perturbations by the core.

Because the molecular core is no longer symmetric, assigning s, p, or d character to a molecular Rydberg state is only qualitative, and Rydberg states with different l but with the same symmetry can interact with each other. Nevertheless, visual inspection of MOs and wave function amplitudes shows that many molecular Rydberg states can indeed be described as s or p or d states. Fig. 13.1 shows Dyson orbitals[59] corresponding to the excited states of the NO dimer[1]. The orbitals are no longer atom-centered, and three p-orbitals are no longer degenerate due to the core asymmetry. However, because the spatial extent of the orbitals is very large relative to the dimer core, they preserve their hydrogen-atom like appearance. For example, one of the A_1 state can be easily identified as an s-like Rydberg state, whereas another A_1 and two B_2 states resemble p orbitals. Note that the spatial extent of the second B_2 state is less than that of the A_1 states, because of its interactions with the valence state of the same symmetry.

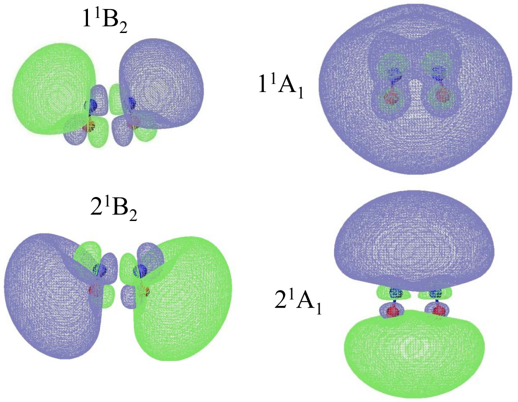


Figure 13.1: Dyson orbitals corresponding to the two B_2 (left) and two A_1 states of $(NO)_2$ (the numbering of the states is not spectroscopic and is only used to distinguish the states, e.g., $1A_1$ state is not the lowest A_1 state of the dimer, rather, the lowest of the two A_1 Rydberg states considered in this example). The B_2 states are of a mixed Rydberg-valence character, whereas the A_1 states are predominantly Rydberg. Note the similarity between the respective Dyson MOs and the hydrogen-atom like orbitals.

We note also the difference in size of low-lying Rydberg and valence states, which can be quantified by expectation values of $\hat{r}^2$. $< r^2 >$ for valence states that involve n, π^* or σ^* are very similar to the ground state values. The difference between the $< r^2 >$ values for the ground and excited states, $\Delta < r^2 >$, provides a better measure of the extent of electronic density in the excited states than just the value of $< r^2 >$, because the latter depends on the molecular size, whereas the former does not, which

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[1] Dyson orbitals allow one to visualize differences between correlated multi-configurational wave functions of the neutral species and the respective cations, and are particularly useful when analyzing electron distributions in excited states.

enables comparisons between molecules of different sizes. In small molecules, the typical values of $< r^2 >$ are 10-12 $(\text{Å})^2$, and the change in $< r^2 >$ upon excitation from the ground to a valence state,$\Delta < r^2 >$, is less that 1 $(\text{Å})^2$, whereas for the $3s$ or $3p$ Rydberg state $\Delta < r^2 >$ are about 12 $(\text{Å})^2$.

This can serve as another basis of identification and assignments of Rydberg states (see, for example, assignment of Rydberg and valence states of diazomethane in Ref. 60). Rydberg-valence state interactions are expected to transpire in the region closest to the core, affecting vibrational levels as well.

13.4.4 Performance of the CIS model

What are the limitation for CIS?

- Neglect of non-dynamical correlation for the ground state: as the HF model, CIS will break when HF description fails. Examples: dissociation curves by CIS.

  PICTURE HERE

  This is even more frustrating than HF behavior, because often excited states minima corresponds to the significant geometry changes of the excited molecule, i.e., bond breaking. Hence, often CIS can break at the stationary points on the excited state — even though HF would be a good wavefunction at the ground state equilibrium geometry.

  However, CIS includes some non-dynamical correlation, for example, it can describe singly excited states which are linear combination of two determinants, such as singly excited Σ_u state of H_2.

- Related problem arises when there is (near)-degeneracy obtained at CIS level. Nearly degenerate CIS states can strongly mix when correlation is included, hence, they can change considerably. Such states are of questionable accuracy.

- Cannot describe doubly and other multiply excited states. However, they are important. Also, they can mix with singly excited states and to change them considerably. Example: A_g, B_u states of butadiene and hexatriene.

- The lack of dynamical correlation. This can yield errors of 1 eV even if CIS wavefunction is qualitatively correct. This effect (changes in non-dynamical correlation upon excitation) is called differential correlation effects. Why does non-dynamical correlation changes? We separate electron pair by promoting one electron up.

CIS is a semi-quantitative model. Errors can be as large as 1.5 eV, but the ordering of the states is often OK. So, it is inexpensive (scaling is N^5 due to integral transformation) model for qualitative analysis.

The attractive features of CIS: the model is size-extensive (as the HF model itself) and predictive (does not require any extra input).

Why is it size-extensive? Because we have only single excitations, and for the separated fragments these excitations can be on one fragment only. It is variational — in some sense.

13.5 CIS(D) models

One possibility to improve CIS model is to include dynamical correlation correction similar to MP2 model for the ground state.[61,62] As far as PT is concerned, there are two distinct situations: degenerate and nondegenerate PT. In case of degeneracy, we cannot just correct energies of individual states, but have to re-diagonalize perturbed degenerate blocks.

Consider first MP2 correction for the ground state energy:

$$E =< \Phi_0|V|T_2\Phi_0 >, \tag{13.23}$$

where V is a fluctuation potential ($V = H - F$), and T_2 are double excitation operator. We have seen that first order corrections to the zero-order wavefunction include only T_2, and which are defined from:

$$< \Phi_{ij}^{ab}|F + V - E_0|T_2\Phi_0 >= 0 \tag{13.24}$$

Similarly, PT can be applied to CIS states ($\Psi_{CIS} = U_1\Phi_0 = \sum_{ia} u_i^a \Phi_i^a$). CIS equations are:

$$< \Phi_i^a|F + V - E|U_1\Phi_0 >= \omega u_i^a \tag{13.25}$$

Consider first CIS-MP2 corrections. This theory is based on the assumption that similar physics holds for the excited states, with two modifications relative to MP2. First, double substitutions from CIS give triple excitations from the Φ_0, and, second, Brillouin's theorem does not hold for CIS, thus we must also include single substitutions from CIS, which are double excitations from the reference HF determinant. Corrections are:

$$E_{CIS-MP2} =< \Psi_{CIS}|V|U_2\Phi_0 > + < \Psi_{CIS}|V|U_3\Phi_0 > \tag{13.26}$$

U_2 and U_3 equations are found from first order PT expressions for the CIs wavefunctions, and they a set of equations should be solved to define these amplitudes. This is computationally demanding (scaling is N^6, as for CCSD). Moreover, these corrections are not size-extensive!

CIS(D) model takes care of these problems. Again, we are considering nondegenerate case. CIS(D) approximates U_3 term by product of T_2U_1, where T_2 are ground state MP2 amplitudes and U_1 are CIS amplitudes, thus assuming that for "inactive" electrons correlation effects do not change upon excitation.

$$E_{CIS(D)} =< \Psi_{CIS}|V|U_2\Phi_0 > + < \Psi_{CIS}|V|U_1T_2\Phi_0 > \tag{13.27}$$

The scaling of CIS(D) is N^5 and it is size-extensive!

Performance of CIS(D) model is greatly improved. (DISCUSS TABLES). (02.-0.5 eV for many cases where CIS errors were of 1.5 eV). There is, however, important problem associated with degeneracy. We do not expect this theory based on non-degenerate PT theory to work well when zero-order states are degenerate. What to do? This questions consists of two: (i) How do we know where CIS(D) unreliable? (ii) How do we correct it?

There is simple diagnostic (θ diagnostic) for CIS(D) model. It estimates maximum possible mixing of the zero-order CIS state with other states expressed in terms of angle (Givens rotations). When this angle is large, then CIS(D) is unreliable.

Theory which corrects CIS(D) for degeneracy: CIS(D_1) model. Performs better for degenerate situations.

SOS-CIS(D) method:[63] very fast and surprisingly accurate.

13.6 Higher order CI

The question now is — can we systematically improve CIS model? Can we, for example, include all double excitations as well?

PICTURE OF FCI AGAIN.

The answer is not quite. Though from VP we know that by expanding our linear subspace (defined by many electron basis set) we will get closer and closer to the exact energies, our transition energies can become worse. How? Because we know nothing about how fast each of the CI roots approaching exact solution. And that is exactly the case. Consider CISD. Doubles are coupled to the Φ_0. Which means that our CISD ground state wf will include all double excitations fro m Φ_0. However, since triples are not included, excited state wavefunction does not include double excitations. This results in non-balanced description of the excited and ground state. CIS excitation energies are usually much more accurate than those of CISD.

Chapter 14

Equation-of-Motion methods for open-shell and electronically excited species

This chapter is based on References 64, 65. There is a more recent and more focused review on EOM-CC approaches which I am going to use for lectures – Ref. 66.

14.1 Introduction

High-level calculations of closed-shell molecules can now be carried out almost routinely due to the availability of efficient and user-friendly electronic structure packages featuring a hierarchy of "theoretical model chemistries".[9] The well-defined nature of these approximate methods of solving electronic Schrödinger equation enables their calibration[3] thus providing error bars for each model. By using these error bars as criteria for balancing accuracy versus computational cost, a chemist can choose just the right tool for a particular problem at hand, and use it in a "black box" fashion.

As defined by Pople, "theoretical model chemistry" consists of a pair of well-defined approximations to the exact wavefunction: correlation treatment and one-electron basis set.[9] Fig. 14.1 summarizes a hierarchy of approximate methods for correlation treatment[?, 3, 67] in the ground and excited states. Both the ground and excited states' series converge to the exact solution, and the accuracy of the description improves with each additional step of sophistication (at the price of increased computational cost, of course). Fortunately, chemically and spectroscopically relevant answers can be obtained within computationally tractable (for moderate-size molecules) models. For example, the coupled-cluster model with single and double excitations[68] augmented by triple excitations treated perturbatively [CCSD(T)][69] yields highly accurate structural (errors in bond lengths of 0.002-0.003 Å) and thermochemical (errors of less than 1 kcal/mol in reaction enthalpies) data.[3] Excitation energies can be calculated with 0.1-0.3 eV accuracy[70] by the excited states' counterpart of CCSD, equation-of-motion for excitation energies (EOM-EE) CCSD method.[71–73] Note that *multi-configurational* excited states, e.g., open-shell singlets, are correctly described

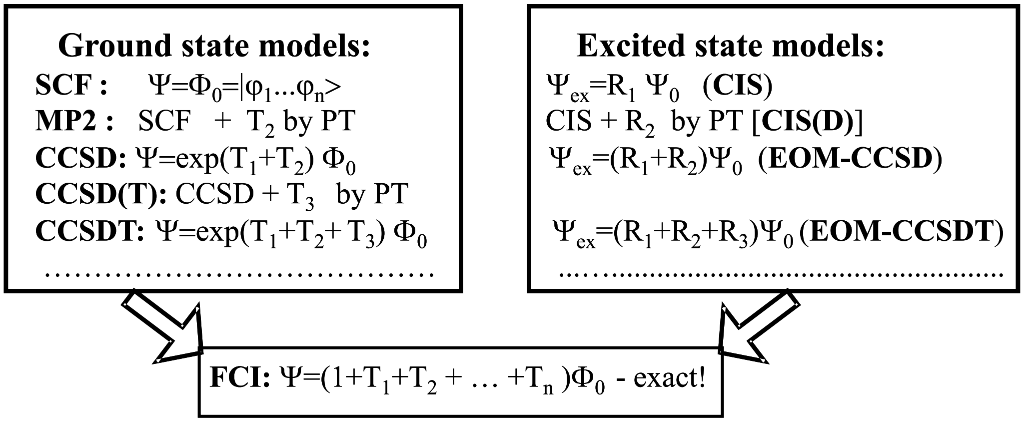

Figure 14.1: The hierarchy of approximations to an N-electron wavefunction. Models of increasing complexity for ground and excited state wavefunctions are presented in the left and right panels, respectively. The simplest description of an N-electron wavefunction is given by a single Slater determinant composed of spin-orbitals, i.e., states of pseudo-independent electrons moving in the field of nuclei and a mean field of other electrons [self-consistent filed (SCF), or Hartree-Fock (HF) model]. The effects of electron interaction, i.e., correlation, can gradually be turned on by including single, double, and higher excitations (T_1, T_2, etc). This can be done perturbatively, e.g., as in the Møller-Plesset theory (MP), or explicitly, e.g., as in coupled-cluster (CC) methods. The corresponding excited states' models can be derived within the linear response (LR) or equation-of-motion (EOM) formalisms, in which the excited states are described as electronic excitations from approximate ground state wavefunctions (the operator R_m generates all possible m-electron excitations out of the reference determinant Φ_0). For example, the SCF analog for excited states, the configuration interaction singles (CIS) model, describes excited states as a linear combination of all singly excited determinants. Similarly to the ground state models, accuracy can systematically be improved by including higher excitations. Both series converge to the exact solution of the Schrödinger equation (in a given one-electron basis set) — full configuration interaction (FCI), which, in turn, becomes exact in the limit of the complete one-electron basis set.

by the *single-reference* (SR) excited state models, provided that their wavefunctions are dominated by single-electron excitations. For example, the two-configurational $^{1,3}\pi \rightarrow \pi^*$ excited states of ethylene are correctly described even at the CIS level, since both configurations, $\pi\alpha\pi^*\beta$ and $\pi\beta\pi^*\alpha$, are single-electron excitations from the ground state $\pi\alpha\pi\beta$ determinant.

Unfortunately, *the above error bars are valid only for species whose ground state wavefunction is dominated by a single Slater determinant and for excited states dominated by single electron excitations.* This restricted the mainstream applications of SR models to well-behaved molecules such as closed-shell species at their equilibrium geometries, some doublet radicals, or triplet diradicals, leaving many chemically important situations (e.g., transition states, bond-breaking, singlet diradicals[74] and triradicals) to the domain of multi-reference methods.[75, 76]

To understand the origin of the breakdown of the SR methods away from equilibrium, consider the torsional potential in ethylene (Fig. 14.2). Whereas at its equilibrium geometry ethylene is a well-behaved closed-shell molecule whose ground and π-valence excited states can be described accurately by SR models (except for the doubly excited Z-state), it becomes a diradical at the barrier, when the π-bond is completely broken.[77] Thus, at the twisted geometry all of ethylene's π-valence states (N, T, V, and Z) are two-configurational, *except for the high-spin components of the triplet.*

The traditional recipe for computing ethylene's torsional potential for the ground and excited states would involve state-by-state (or state-averaged) calculations with the two-configurational SCF (TCSCF) method, the simplest variant of complete active space SCF (CASSCF) further augmented by perturbation theory (MRPT) or configuration interaction (MRCI) corrections.[75] Similar ideas have also been explored within CC formalism.[30, 78–80]

Here we discuss an alternative strategy, the spin-flip (SF) approach, which is, as any EOM model, a multi-state method (i.e., yields several states in one computation), does not require an active space selection and orbital optimization (thus, is genuinely a robust "black-box" type SR method), and treats both non-dynamical and dynamical correlation simultaneously (i.e., is not a two-step procedure).

As mentioned above, the M_s=±1 components of the T-state of ethylene (Fig. 14.2) are single-determinantal at the ground state equilibrium geometry, and remain single-determinantal at all values of the twisting angle. Therefore, they can be accurately described by SR methods at all the torsional coordinates.[81] Moreover, all the low-spin M_s=0 determinants from Fig. 14.2 are formally *single-electron excitations from the high-spin triplet state involving a spin-flip of one electron.* This immediately suggests employing EOM or LR formalism and describing the target $M_s = 0$ states as spin-flipping excitations from the well-behaved high-spin reference state. This is the essence of the SF approach[82–88] described below.

14.2 Equation-of-motion: A versatile electronic structure tool

EOM approach[?, 71, 73, 87, 89–91] is a powerful and versatile electronic structure tool that allows one to describe many multi-configurational wavefunctions within a single-reference formalism.[92] Conceptually, EOM is similar to configuration interaction (CI): target EOM states are found by diagonalizing the so-called similarity transformed Hamiltonian $\bar{H} \equiv e^{-T} H e^{T}$:

$$\bar{H} R = E R, \tag{14.1}$$

where T and R are general excitation operators w.r.t. the reference determinant $|\Phi_0>$. Regardless of the choice of T, the spectrum of $\bar{H}$ is exactly the same as that of the original Hamiltonian H — thus, in the limit of the complete many-electron basis set, EOM is identical to FCI. In a more practical case of a truncated basis, e.g., when T and R are truncated at single and double excitations, the EOM models are numerically

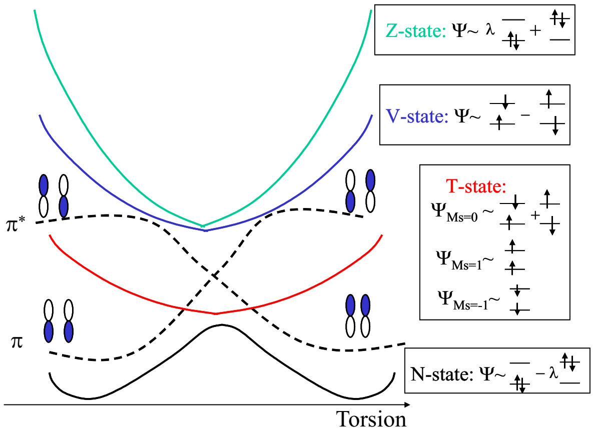

Figure 14.2: Around equilibrium, the ground state (N-state) wavefunction of ethylene is dominated by the π^2 configuration. However, as a degeneracy between π and π^* develops along the torsional coordinate, the importance of the $(\pi^*)^2$ configuration increases. At the barrier, where π and π^* are exactly degenerate, the qualitatively correct wavefunction for the N-state must include both configurations with equal weights. That is why the quality of the SR wavefunctions degrades as the molecule is twisted: even when the second configuration is explicitly present in a wavefunction (e.g., as in the CCSD or CISD models), it is not treated on the same footing as the reference configuration, π^2. The singlet and triplet $\pi\pi^*$ states (the V and T states, respectively) are formally single-electron excitations from the N-state, and are well described by the SR excited states' models (despite the fact that both the singlet and the M_s=0 component of the triplet are two-configurational and therefore are not accessible by the ground state SR methods). The Z-state, however, is formally a doubly-excited state with respect to the N-state, and therefore SR models will not treat it accurately. Note that the high-spin $M_s = \pm 1$ components of the triplet T-state remain single-determinantal at all the torsional angles. Moreover, all the $M_s = 0$ configurations employed in the N, V, T, and Z states are formally single-electron excitations which involve a spin-flip of one electron with respect to any of the two high-spin triplet configurations.

superior to the corresponding CI models,[93] because correlation effects are "folded in" in the transformed Hamiltonian. Moreover, the truncated EOM models are rigorously size-extensive,[94,95] provided that the amplitudes T satisfy the CC equations for the reference state $|\Phi_0>$:

$$< \Phi_\mu|\bar{H}|\Phi_0 >, \tag{14.2}$$

where Φ_μ denotes μ-tuply excited determinants, e.g., $\{\Phi_i^a, \Phi_{ij}^{ab}\}$ in the case of CCSD.

The computational scaling of EOM-CC and CI methods is identical, e.g., both EOM-CCSD and CISD scale as N^6. By combining different types of excitation operators and references $|\Phi_0>$, different groups of target states can be accessed as explained in Fig. 14.3. For example, electronically excited states can be described when the reference $|\Phi_0>$ corresponds to the ground state wavefunction, and operators R conserve the number of electrons and a total spin.[71–73] In the ionized/electron attached EOM models,[96–98] operators R are not electron conserving (i.e., include different number of creation and annihilation operators) — these models can accurately treat ground and excited states of doublet radicals and some other other open-shell systems. For example, singly ionized EOM methods, i.e., EOM-IP-CCSD and EOM-EA-CCSD, have proven very useful for doublet radicals whose theoretical treatment is often plagued by symmetry-breaking. Finally, the EOM-SF method[82,87] in which the excitation operators include spin-flip allows one to access diradicals, triradicals, and bond-breaking without using spin- and symmetry-broken UHF references.

To summarize, the EOM approach enables one to describe many *multi-configurational* wavefunctions within a *single-reference* formalism. The EOM models are rigorously size-extensive, and their accuracy can be systematically improved (up to the exact FCI results) by including higher excitations explicitly or perturbatively. Moreover, the EOM methods are *multi-state* schemes — several target states are obtained in the single diagonalization step. This results in an improved accuracy due to the built-in error cancellation and greatly simplifies the calculation of coupling elements, such as non-adiabatic or spin-orbit couplings, between the states. Simpler formalism also facilitates implementation of analytic gradients and properties calculations[73,96,99,100]

14.3 The spin-flip method

In traditional (non-SF) SR excited states EOM models, the excited state wavefunctions are parameterized as follows (see Fig. 14.1):

$$\Psi^{s,t}_{M_s=0} = \hat{R}_{M_s=0}\tilde{\Psi}^{s}_{M_s=0}, \tag{14.3}$$

where $\tilde{\Psi}^{s}_{M_s=0}$ is a closed-shell reference wavefunction, and the operator $\hat{R}$ is an excitation operator truncated at a certain level of excitation consistent with the theoretical model employed to describe the reference state. Note that only excitation operators that do not change the total number of α and β electrons, i.e. M_s=0, need to be considered in Eq. (14.3).

As explained in the Introduction, this scheme breaks down both for ground and excited states when orbitals from occupied and virtual subspaces become near-degenerate, e.g. at the dissociation limit or in diradicals (see Fig. 14.2). To overcome this problem, the SF model employs a high-spin triplet reference state, which is accurately described by a SR wavefunction. The target states, closed- and open-shell singlets and triplets, are described as spin-flipping excitations:

$$\Psi^{s,t}_{M_s=0} = \hat{R}_{M_s=-1}\tilde{\Psi}^{t}_{M_s=+1}, \tag{14.4}$$

where $\tilde{\Psi}^{t}_{M_s=+1}$ is the $\alpha\alpha$ component of the triplet reference state, $\Psi^{s,t}_{M_s=0}$ stands for the final (M$_s$=0) singlet and triplet states, respectively, and the operator $\hat{R}_{M_s=-1}$ is an excitation operator that flips the spin of an electron. As can be seen from Fig. 14.2, all the configurations used to describe diradical-type wavefunctions (e.g., N, V, T, and Z states of ethylene) are formally single excitations with respect to the high-spin component of the triplet ($|\pi\alpha\pi^*\alpha>$).

Fig. 14.4 shows the reference high-spin configuration and the spin-flipping single and double excitations for four electrons in four orbitals system. The first configuration in the second row corresponds to a ground-state closed shell singlet. It is followed by the configuration that becomes degenerate with it at the dissociation limit. Two next configurations complete a set necessary to describe all diradicals' states, e.g., states which can be derived by distributing two electrons over two (nearly) degenerate orbitals (N, V, T, and Z states of twisted ethylene are of this type). It is easy to see that these four configurations are treated on an *equal footing* in our model, and that other configurations *do not introduce imbalance in their treating*.

Therefore, the SF ansatz (14.4) is sufficiently flexible to describe changes in ground state wavefunctions along a single bond-breaking coordinate. Moreover, it treats both closed-shell (e.g., N and Z) and open-shell (V and T) diradicals' states in a balanced fashion, i.e., without overemphasizing the importance of one of the configurations.

Note that the SF set of determinants is not a spin-complete set. Whereas all the closed-shell and open-shell diradical configurations appear as single excitations (first four in the second row in Fig. 14.4), the counterparts of other single SF determinants (i.e., those which include excitations of electrons from doubly occupied or to the unoccupied MO's) are formally double or triple excitations. Thus, when all singles and doubles are included into the SF model, the resulting wavefunctions are not eigenstates of S^2, i.e., are spin-contaminated. However, the spin-contamination is rather small — because the SF excitations within the open-shell form a spin-complete set. For example, the values of $< S^2 >$ for the X^3B_1, $\tilde{a}^1A_1$, $\tilde{b}^1B_1$, and $\tilde{c}^1A_1$ states of methylene at their equilibrium geometries are 1.9991, -0.0011, -0.0007, and -0.0007, respectively, at the EOM-SF-CCSD/TZ2P level using UHF reference. The spin-completeness of SF models can be achieved by including a subset of higher excitations.[88] Although this increase a computational cost of a model, the scaling remains the same.[88] Most importantly, the size-extensivity of SF models is not violated as a result of extending the determinantal subspace.

Similarly to traditional excited state theories, the description of the final states can be systematically improved by employing theoretical models of increasing complexity for the reference wavefunction as summarized in Fig. 14.5. For example, the simplest SF model employs a Hartree-Fock wavefunction, and the operator $\hat{R}$ is then truncated at single excitations (SF-CIS or SF-SCF).[82,88] SF-CIS can be further augmented by perturbative corrections [SF-CIS(D) or SF-MP2].[83] A yet more accurate description can be achieved by describing the reference wavefunction by a coupled-cluster model, e.g., CCSD[87] or OO-CCD.[82,101] In this case, the excitation operator $\hat{R}$ consists of single and double excitation operators involving a flip of the spin of an electron.[82] Finally, inclusion of triple excitations in the EOM operator R results in the EOM-SF(2,3)[102] model, which is capable of chemical accuracy. The corresponding SF equations in spin-orbital form are identical to those of traditional excited state theories, i.e., CIS, CIS(D), EOM-EE-CCSD or EOM-EE-OOCCD, and EOM-EE(2,3), however, they are solved in a different determinantal subspace: non-SF theories consider only M_s=0 excitation operators, whereas SF operates in the M_s=-1 subspace. The computational cost and scaling of the SF models are identical to those of the corresponding non-SF excited state theories.

Two of the SF models, SF-CISD and SF-DFT, deserve special mention. By using the SF approach, CI can be formulated in a rigorously size-extensive way.[84,88,94] For example, the SF-CISD model is (i) variational, (ii) size-consistent, and (iii) exact for two electrons thus simultaneously satisfying these three highly desirable properties.[9]

Lastly, the SF approach implemented within the time-dependent (TD) density functional theory (DFT) extends DFT to multi-reference situations with no cost increase relative to the non-SF TD-DFT. Similarly to DFT and TD-DFT, the SF-DFT model[86] is formally exact and therefore will yield exact answers with the exact density functional. With the available inexact functionals, the SF-DFT represents an improvement over its non-SF counterparts, e.g., it yields accurate equilibrium properties and singlet-triplet energy gaps in diradicals.[86] All of the above SF models, as well as the corresponding spin-conserving models and analytic gradients for SF-CIS, SF-TDDFT, and EOM-EE/SF-CCSD[100] are implemented in the *Q-CHEM* electronic structure package.[103]

14.4 The spin-flip method for bond-breaking: the ethylene torsional potential

Fig. 14.6 shows the torsional potential calculated by the SF [SF-CIS, SF-CIS(D), and SF-OD] and non-SF (restricted and unrestricted HF and OD) methods.[82,83,104] All curves are compared with the TC-CISD curve.[83] The unbalanced treatment (within a single reference framework) of $(\pi)^2$ and $(\pi^*)^2$ configurations results in unphysical shapes of the PES, i.e., a cusp at 90^o and large errors in barrier heights. The spin-unrestricted PESs are smooth; however, the barrier height is usually underestimated, even by the highly correlated methods.[104] Moreover, the shape of the unrestricted PES can be quite wrong, for example, the U-OD curve is too flat around the barrier as compared against the TC-CISD one (see Fig. 14.6). Also, the UHF based wavefunctions are heavily spin-contaminated around the barrier *even for highly correlated methods such as coupled-cluster models*.[104] All the SF models produce smooth PESs. Quantitatively, SF-SCF represents a definite advantage over both the RHF and UHF results. Similarly, the SF-OD curve is closer to our reference TC-CISD curve than either R-OD or U-OD. The SF-CIS(D) curve is very close to the more expensive SF-OD one. Similar performance of the SF methods has been observed for bond-breaking in HF, BH, and F_2.[82–84]

14.5 The spin-flip method for diradicals

Diradicals[25,74,105] represent the most clear-cut application of the SF approach because in these systems the non-dynamical correlation derives from a single HOMO-LUMO pair (e.g., π and π^* in twisted ethylene). In this section we present results for trimethylenemethane (TMM), a very challenging case due to the exact degeneracy of its frontier orbitals (for a detailed review of previous TMM studies, see Ref.[106]).

The π-system of TMM is shown in Fig. 14.7: four π-electrons are distributed over four molecular π-type orbitals. Due to the exact degeneracy between the two e' orbitals at the D_{3h} structure, the ground state of TMM is a ${}^3A_2'$ state (similar to the T-state in ethylene), in agreement with Hund's rule predictions.

The vertical excitation energies are summarized in Fig. 14.7 (with C_{2v} symmetry labels).[85,106] The three lowest singlet states are the diradical singlet states (similar to the N, V, and Z states of ethylene). However, excited states that derive from excitations of other π electrons are also relatively low in energy. The first closed-shell singlet, ${}^1A_1$ and the open-shell singlet ${}^1B_2$ (similar to the N and V states of ethylene, respectively) are degenerate at the D_{3h} geometry due to the degeneracy of a_2 and $2b_1$ orbitals (note that CASSCF fails to reproduce this exact degeneracy, unless the state-averaged orbital optimization is performed). The second closed-shell singlet 2^1A_1 (an analog of the Z-state) is followed by a pair of degenerate triplets, ${}^3A_1$ and ${}^3B_2$, obtained by excitation of one electron from the doubly occupied $1b_1$ orbital to the a_2 or $2b_1$ degenerate orbitals. Finally, there is a quintet ${}^5B_2$ state in which all π-orbitals are singly occupied. We do not discuss low-lying states derived from electron excitations beyond the TMM's π-system. Several such states appear between the pair of degenerate triplets and the quintet state. The SF-OD and SF-CCSD models should be augmented by higher excitations to achieve a quantitatively accurate description of these states.[102]

In accordance with the Jahn-Teller theorem, the degeneracy between the degenerate states (closed-shell and open-shell singlets, and a pair of triplets) can be lifted in lower symmetry. The closed-shell singlet is stabilized at the planar C_{2v} geometry, with one short CC bond. The open-shell singlet prefers an equilibrium structure with one long CC bond and a twisted methylene group. The second ${}^1A_1$ state prefers D_{3h} equilibrium geometry. The EOM-SF-CCSD/EOM-SF(2,3) adiabatic singlet-triplet energy separations for the three lowest singlet states are 0.51/0.65 eV, 0.92/0.77 eV, and 4.34/4.03 eV for the 1^1B_1, 1^1A_1, and 2^1A_1 states, respectively[102] (in the basis set composed of the cc-pVTZ basis on carbons and the cc-pVDZ basis on hydrogens). These energies are very close to the MRPT values[85] of 0.71 and 0.83 eV (for the 1^1B_1 and 1^1A_1 states, respectively). With regard to experiment, the lowest adiabatic state, 1^1B_1, has not been observed in the photoelectron spectrum[107] because of unfavorable Franck-Condon factors. The experimental adiabatic energy gap (including ZPE) between the ground triplet state and the 1^1A_1 state is 0.70 eV. The estimated experimental T_e is 0.79 eV, which is in excellent agreement with the EOM-SF(2,3) estimate.

In our detailed benchmarks study,[85,102] we calculated the singlet-triplet energy separations for a large number of systems, i.e., O,C, and Si atoms, O_2, NH, NF, and OH^+ diatomics, methylene isovalent series (CH_2, NH_2^+, SiH_2, and PH_2^+), benzynes, and TMM. In all these cases, the SF models performed very well. The typical errors for EOM-SF-OD/EOM-SF-CCSD are less than 1 kcal/mol, and the maximum error was 3 kcal/mol, as compared to the experimental or highly accurate multi-reference values. Inclusion of triples in the EOM part brings the error bars down to hundredths of eV.

14.6 Trirdicals

Triradicals[108–111] — species with three unpaired electrons distributed over three nearly degenerate orbitals — feature even more extensive electronic degeneracies than diradicals. Fig. 14.8 shows valid triradical wavefunctions with a positive projection of the total spin, i.e., with $M_S=+\frac{3}{2},\frac{1}{2}$. Note that only the high-spin component of the quartet state, the first configuration in Fig. 14.8, is single-configurational, while all the low-spin states are multi-configurational and are, therefore, not accessible by the traditional ground state single-reference methods. However, all these states can accurately be described by the SF models as:

$$\Psi^{d,q}_{M_S=1/2} = \hat{R}_{M_S=-1}\tilde{\Psi}^{q}_{M_S=3/2}, \tag{14.5}$$

where $\tilde{\Psi}^{q}_{M_S=3/2}$ is the $\alpha\alpha\alpha$ high-spin reference determinant, $\hat{R}_{M_S=-1}$ is an excitation operator that flips the spin of an electron ($\alpha \to \beta$), and $\Psi^{d,q}_{M_S=1/2}$ stands for the wavefunctions of the doublet and quartet target states. Since all the configurations (with $M_S = 1/2$) present in the low-lying triradical states are formally obtained from the $M_S = 3/2$ reference state by single excitations including a spin-flip, the SF method provides a balanced description of all the triradical states from Fig. 14.8.

Note that, although all the target states – the quartet, the open-shell doublets and and the closed-shell doublets – are multi-configurational, they are treated by SF within a single-reference formalism.

The SF method enabled recent studies of electronic structure of triradicals.[109–111] These works focused on interactions between the radical centers in finite size molecules and structural, spectroscopic, and thermochemical signatures of these interactions. For example, we have found that there is a bonding interactions between radical centers in the C_6H_3 isomers that results in considerably tighter equilibrium geometries (i.e., the distance between radical centers contracts by 0.05 Å relative to the parent benzene molecule) and higher vibrational frequencies.[109,110] The energies of these interactions vary between 0.5 kcal/mol to up to 37 kcal/mol that constitutes approximately one third of a normal chemical bond.[110] These bonding interactions also determine the multiplicity of the ground state — in all three isomers, multiplicity of the ground state is doublet.

In the 5-dehydro-m-xylylene (DMX) triradical[111] shown in Fig. 14.9, the interaction between radical centers is rather weak due to the σ-π character of the orbitals that host the unpaired electrons. Overall, the interaction between the centers results in an unusual electron arrangement — the ground state of DMX is an *open-shell doublet* state, i.e., the three unpaired electrons are localized at their radical centers, and, contrary to Hund's rule, are coupled antiferromagneticaly. Low lying electronic states of DMX are shown in Fig. 14.10. The dense nature of the DMX electronic spectrum renders MR calculations of this system extremely difficult.

14.7 Conclusions

The realm of HF→MP2→CCSD→CCSD(T)→CCSDT→ … hierarchy of approximations to the exact many-electron wavefunction ends when a wavefunction acquires considerable multi-configurational character, e.g. due to small HOMO-LUMO gap at a dissociation limit, or in electronically excited states. Traditionally, these and other chemically important situations were treated by multi-reference methods that must be tailored to suit a specific problem at hand. The single-reference EOM-CC theory offers an alternative approach to multi-configurational wavefunctions, which truly complies with a set of Pople's attributes of a "theoretical model chemistry". The EOM-CC methods are rigorously size-extensive, include both dynamical and non-dynamical correlation in a balanced fashion, and describe several electronic states in a single computational scheme. Recently, we introduced a new EOM method, EOM-SF, that extended the applicability of SR EOM-CC methods to bond-breaking, diradicals, and triradicals. Both closed and open shell type target states are described within a single reference formalism as spin-flipping, e.g., $\alpha \rightarrow \beta$, excitations from the high-spin triplet (M_s=1) or quartet(M_s=3/2) reference state for which both dynamical and non-dynamical correlation effects are much smaller than for the corresponding low-spin states. Formally, the new theory can be viewed as an EOM model where the excited states are sought in the basis of determinants conserving the total number of electrons but changing the number of α and β electrons.

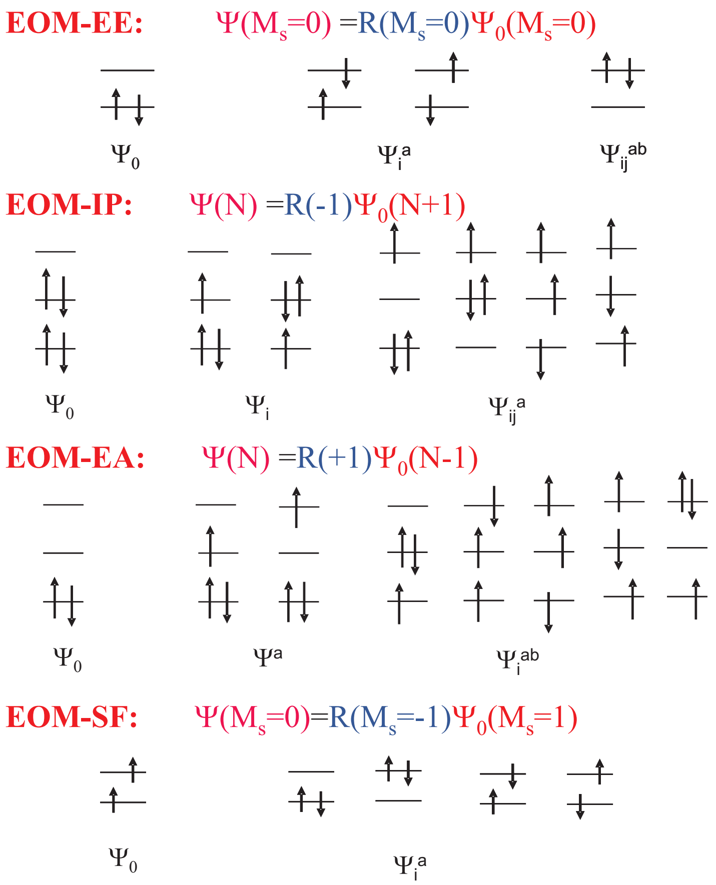

Figure 14.3: In EOM formalism, target states Ψ are described as excitations from a reference state Ψ_0: $\Psi = R\Psi_0$, where R is a general excitation operator. Different EOM models are defined by choosing the reference and the form of the operator R. In the EOM models for electronically excited states (EOM-EE, upper panel), the reference is the closed-shell ground state Hartree-Fock determinant, and the operator R conserves the number of α and β electrons. Note that two-configurational open-shell singlets are correctly described by EOM-EE since both leading determinants appear as single electron excitations. However, EOM-EE fails when a small HOMO-LUMO gap causes the ground state wavefunction to be a mixture of two closed-shell determinants (the reference and the doubly excited one): although both determinants may be present in the target wavefunction, they are not treated on an equal footing. The second and third panels present the EOM-IP/EA models. The reference states for EOM-IP/EA are determinants for $N + 1/N - 1$ electron states, and the excitation operator R is ionizing or electron-attaching, respectively. Note that both the EOM-IP and EOM-EA sets of determinants are spin-complete and balanced w.r.t. the target multi-configurational ground and excited states of doublet radicals. Finally, the EOM-SF method (the lowest panel) employs the hight-spin triplet state as a reference, and the operator R includes spin-flip, i.e., does not conserve the number of α and β electrons. All the determinants present in the target low-spin states appear as single excitations, which ensures their balanced treatment both in the limit of large and small HOMO-LUMO gaps.

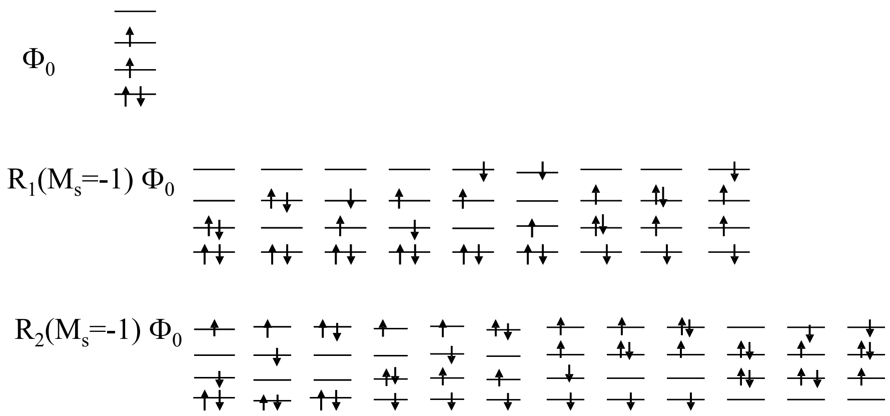

Figure 14.4: Four electrons in four orbitals system. Configuration Φ_0 is the reference configuration. Single-electron excitations with spin-flip produce configurations in the first row. Two-electron excitations with a single spin-flip produce configurations in the second row. Note that non-spin-flipping excitations or excitations that flip the spin of two electrons produce $M_s=\pm1$ configurations, which do not interact through the Hamiltonian with the final $M_s=0$ states, and thus are not present in the model.

Reference:	**Method:**	**Wavefunction:**
SCF	SF-SCF (or SF-CIS)	$R_1\ \Phi_0$
MP2	SF-MP2 [or SF- CIS(D)]	$R_1\ \Phi_0 + T_2$ by PT
CCSD	EOM-SF-CCSD	$(R_1+R_2)\exp(T_1+T_2)\Phi_0$
CCSDT	EOM-SF-CCSDT	$(R_1+R_2+R_3)\exp(T_1+T_2+T_3)\Phi_0$

Figure 14.5: Hierarchy of the SF models. Similarly to the non-SF SR methods, the SF models converge to the exact n-electron wavefunction when the spin-flipping operator $\hat{R}$ includes up to n-tuple excitations. For example, the EOM-SF-CCSD model is exact for two electrons.

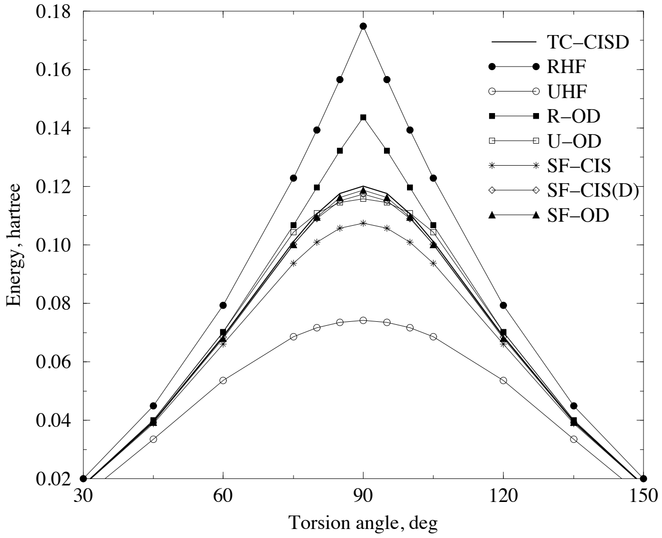

Figure 14.6: Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0^o is zero. The spin-flip curves do not exhibit an unphysical cusp and are closer to the reference TC-CISD curve than the corresponding spin-restricted and spin-unrestricted models.

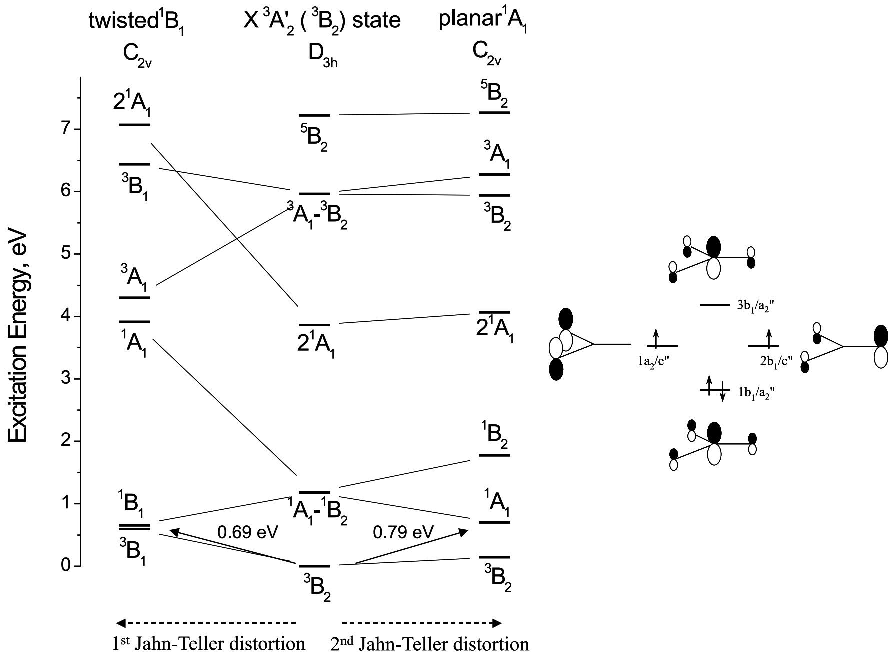

Figure 14.7: On the right, the π-system of TMM and the electronic configuration of the ground state are shown (C_{2v} labels are used). The left panel presents electronic states of TMM at the ground state equilibrium D_{3h} geometry, and at the two Jahn-Teller C_{2v} distorted structures (equilibrium geometries of the 1^1B_1 and 1^1A_1 states). The corresponding adiabatic singlet-triplet gaps are also shown.

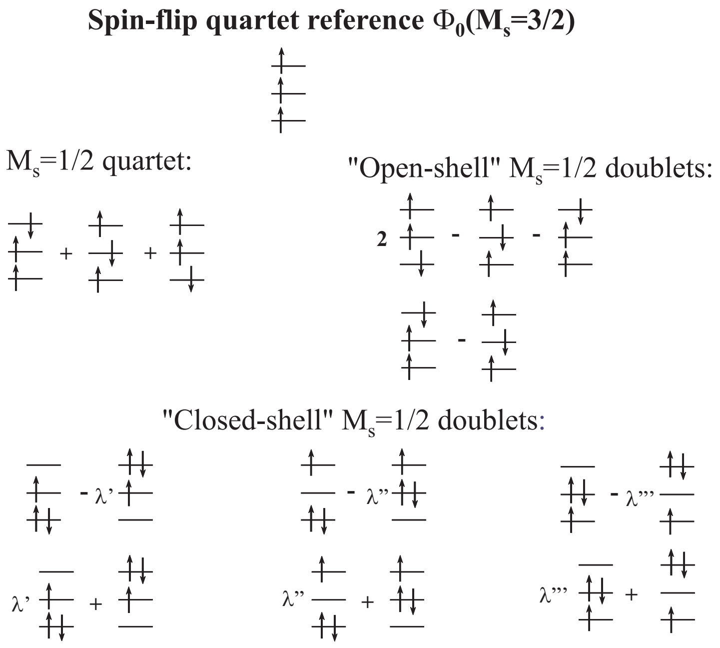

Figure 14.8: Triradicals' wavefunctions that are eigenfunctions of $\hat{S}^2$. Note that all the $M_s = 1/2$ configurations present in the low-lying triradical states are formally obtained from the $M_s = 3/2$ reference state by single excitations including a spin-flip. The coefficients λ that define the mixing of closed-shell determinants depend on the energy spacing between the orbitals, while the coefficients of the open-shell determinants are determined solely by the spin-symmetry requirements. Spatial symmetry determines further mixing of the above wavefunctions.

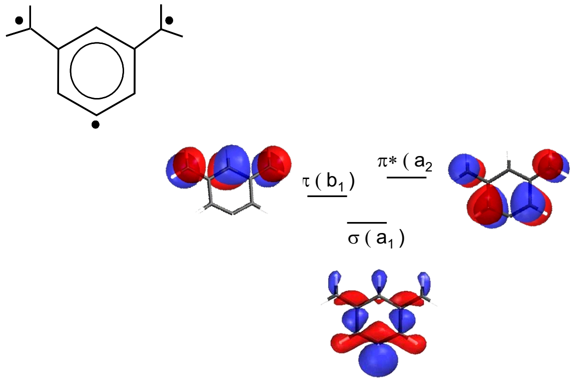

Figure 14.9: Structure and molecular orbitals of DMX.

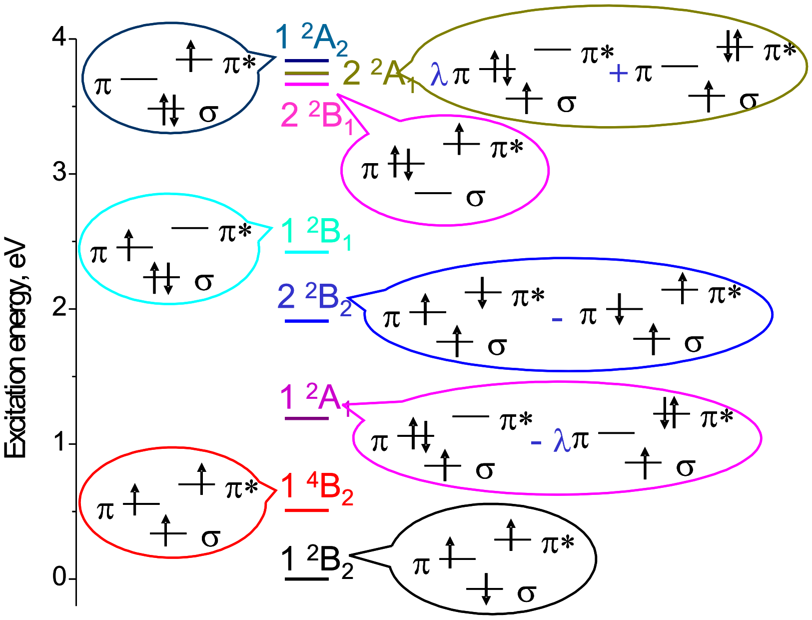

Figure 14.10: Low lying electronic states of DMX. Note that the closed-shell doublet (1^2B_2 state) in which electrons are distributed in accordance with Aufbau principle is 2.5 eV above the ground state. Another likely candidate for the ground state, the quartet 1^4B_2 state, is 0.5 eV above the open-shell doublet, thus violating Hund's rule.

Chapter 15

Excited states: old notes

15.1 Variational Principles for excited states

How can we estimate energies of the excited states?

15.1.1 VP for the ground state

For ground state energy, we have VP: for any trial wavefunction $\tilde{\Psi}$, such that $<\tilde{\Psi}|\tilde{\Psi}>=1$

$$\tilde{E} =<\tilde{\Psi}|H|\tilde{\Psi}>\geq E_0 \tag{15.1}$$

Moreover, if the $\tilde{E}=E_0$, $\tilde{\Psi}=\Psi$. The closer $\tilde{E}$ is to E_0, the smaller is a difference (in terms of norm) between $\tilde{\Psi}$ and Ψ.

15.1.2 Excited states from VP

Theorem 1

If we have $\Psi_0,\ldots,\Psi_N$, N *exact* lowest eigenvalues, and some $\tilde{\Psi}$ which is orthogonal to these lowest exact eigenfunctions, $<\tilde{\Psi}|\tilde{\Psi}>=1$ and $<\tilde{\Psi}|\Psi_k>=0$, $k=0,\ldots,N$, then:

$$<\tilde{\Psi}|H|\tilde{\Psi}>\geq E_{N+1} \tag{15.2}$$

Proof: if $\Psi_0,\ldots,\Psi_N$ are exact eigenfunctions, then matrix of the Hamiltonian is block-diagonal, there is no coupling between block of $<\Psi_k|H|\Psi_l>$ and the rest of the Hamiltonian. Then for orthogonal function we get a problem in orthogonal subspace, where E_{N+1} is the lowest eigenvalue. This problem is thus equivalent to the ground state problem.

PICTURE HERE: block diagonal Hamiltonian.

If the orthogonality to the exact ground state wavefunction is not satisfied, the only thing we know for sure, that the energy of our trial wavefunction is an upper bound of the ground state energy.

This result is not practical, since we do not know exact ground state wavefunction, but an approximate one only.

When it is useful? When there are symmetry restriction and when excited states are orthogonal to the ground state due to specific symmetry. For example, we can always calculate lowest triplet state for the molecules which ground state is singlet state because the triplet is always orthogonal to exact ground state singlet state due to spin-symmetry. Such calculations can be done by Hartree-Fock model, or by other ground-state methods, exactly as we calculate ground states. The same approach can be applied when when have point group symmetry involved. Consider, for example, water molecule. It belongs to c_{2v} point group. For c_{2v} we have the following irreducible representations (Table 15.1):

Table 15.1: Characters for irreducible representations for c_{2v} point group. Molecule is in the ZOX or ZOY plain such that OZ runs between two hydrogens.

Irrep:	E	C$_2$ (Z-axis)	σ_v (ZOX)	σ'_v (ZOY)
A_1; z	1	1	1	1
B_2; y	1	-1	-1	1
A_2	1	1	-1	-1
B_1; x	1	-1	1	-1

In the minimal basis set, there are the following molecular orbitals: $1a_1, 2a_1, 1b_1, 3a_1, 1b_2$ (occupied) and $4a_1, 2b_1$ (virtual). These are valence orbitals, except for $1a_1$ which is a core $1s$ orbital of oxygen. Ground state belongs to the fully symmetric irrep A_1 (this is always a case for closed shell molecule — because doubly occupied orbital is always fully symmetric). Consider now singly excited valence states. We shall use very qualitative description and describe them as one-electronic excitations described by a single substituted Slater determinant. Such description is very crude and would not give even qualitatively correct energies (let alone that we disregard Rydberg states!), but we can use it to analyze symmetry of the valence states. Possible valence single excitations are listed in Table 15.2.

Table 15.2: Symmetries of valence single excitations in water molecule.

Excitation	Symmetry
$1b_2 \rightarrow 4a_1$	B_2
$1b_2 \rightarrow 2b_1$	A_2
$2(3)a_1 \rightarrow 4a_1$	A_1
$2(3)a_1 \rightarrow 2b_1$	B_1
$1b_1 \rightarrow 4a_1$	B_1
$1b_1 \rightarrow 2b_1$	$1A_1$

Thus, the structure of the Hamiltonian in the basis of these determinants assumes the block diagonal form, and we can use Hartree-Fock (and above) models to describe states of B_1, B_2, and A_2 symmetry (for both singlet and for triplet states). Practically, it is very easy to do with PSI, where we can require proper electronic configuration manually (by using *docc* input).

This is not very general approach, since it is limited to the lowest states of the symmetry (and spin-symmetry) other than ground state. Moreover, the quality of such calculations is often lower than quality of the ground state calculations, and therefore there can be very large errors in excitation energies (imbalance and no error cancellation). Why does it happen? Because excited states are often inherently multireference (open shell) states and cannot be described by a single reference models.

Theorem 2

There is, however, stronger result, for Ritz VP. Ritz VP is linear variational principle, when subspace of trial functions is a linear subspace:

$$\tilde{\Psi} = \sum_{k=1}^{N} C_k \tilde{\Psi}_k \tag{15.3}$$

Let us consider Hamiltonian $\tilde{H}$, projected Hamiltonian to the space of trial functions.

$$\tilde{H} = PHP \tag{15.4}$$

$$P = \sum_{k=1}^{N} |\tilde{\Psi}_k >< \tilde{\Psi}_k| \tag{15.5}$$

$$P(\Psi_{\|} + \Psi_{\perp}) = \Psi_{\|} \tag{15.6}$$

P is a projection operator into the space of $\{\tilde{\Psi}_k\}$, $P^2 = P$. We can solve for projected Hamiltonian:

$$\tilde{H}\tilde{\Psi}_k = \tilde{E}_k \tilde{\Psi}_k \tag{15.7}$$

Then we have

$$\tilde{E}_k \geq E_k, \tag{15.8}$$

where E_k are exact energies, and $\tilde{E}_k$ is variational. This is important result which says that we do have some kind of variational estimation for the excited states. Namely, for any linear subspace formed by trial functions, eigenvalues of the Hamiltonian in this subspace gives us upper bounds of corresponding sequential eigenstates of the exact Hamiltonian. Note, however, that exact states which are orthogonal to our trial states will not be described, e.g., if we consider configuration interaction with singly excited states only, doubly excited states would be completely missed. Note also that we can tell nothing about transition energies, $E_k - E_i$, and transition energies are what we want to calculate.

Another result says that if we expand our linear space, our variational energies getting closer to the exact energies. Which means that we can improve our excited state energies by expanding subspace, and that, in principle, we can converge to the exact solutions.

In more rigorous formulation: let us expand our subspace by adding one more function, $\tilde{\Psi}_{N+1}$, orthogonal to the "zero-order" set of trial functions $\tilde{\Psi}_k$, $k = 1, \ldots, N$.

Let us call variational energies for the "zero-order" set of trial functions $\tilde{E}_k^0$, and new variational energies $\tilde{E}_k$. The theorem says that

$$\tilde{E}_0 \le \tilde{E}_0^0 \le \tilde{E}_1 \le \ldots \le \tilde{E}_N^0 \le \tilde{E}_N + 1 \tag{15.9}$$

Proof: Consider our zero-order basis, set of N $\tilde{\Psi}_k$. Let us call projected Hamiltonian (Hamiltonian in the basis of these functions), as $\tilde{H}_0$:

$$\tilde{H}_0 = PHP \tag{15.10}$$

$$P = \sum_{k=1}^{N} |\tilde{\Psi}_k >< \tilde{\Psi}_k| \tag{15.11}$$

$$(\tilde{H}_0)_{ij} =< \tilde{\Psi}_i|H|\tilde{\Psi}_j > \tag{15.12}$$

We can diagonalize $\tilde{H}_0$, and use a new set of its eigenfunctions instead of original $\tilde{\Psi}_k$. Then

$$\tilde{H}_0 = \sum_{k=1}^{N} |\tilde{\Psi}_k >< \tilde{\Psi}_k|\tilde{E}_k^0 \tag{15.13}$$

Secular problem now reads:

$$\begin{pmatrix} \tilde{H}_0 & \boldsymbol{a} \\ \boldsymbol{a}^+ & b \end{pmatrix} \begin{pmatrix} \boldsymbol{C}^0 \\ C \end{pmatrix} = \tilde{E} \begin{pmatrix} \boldsymbol{C}^0 \\ C \end{pmatrix} \tag{15.14}$$

here $\tilde{H}_0$ is the Hamiltonian projected into the space of zero-order trial functions, b is a matrix element for the new added trial function: $b =< \tilde{\Psi}_{N+1}|H|\tilde{\Psi}_{N+1} >$, $\boldsymbol{a}$ represents couplings: $a_k =< \tilde{\Psi}_k|H|\tilde{\Psi}_{N+1} >$, and coefficients $\boldsymbol{C}^0, C$ are coefficient of the new wavefunction:

$$\tilde{\Psi} = \sum_{k=1}^{N} C_k^0 \tilde{\Psi}_k + C\tilde{\Psi}_{N+1} \tag{15.15}$$

This results in the following equations:

$$\tilde{H}_0 \boldsymbol{C}^0 + C\boldsymbol{a} = \tilde{E}\boldsymbol{C}^0 \tag{15.16}$$

$$\boldsymbol{a}^+ \boldsymbol{C}^0 + bC = \tilde{E}C \tag{15.17}$$

$$\tag{15.18}$$

We can now find $\boldsymbol{C}^0$ from the first equation, substitute into second, and cancel number C. Then we can use the fact that $\tilde{H}_0$ is diagonal to take inverse operator:

$$\boldsymbol{C}^0 = -(\tilde{H}_0 - \tilde{E})^{-1} C\boldsymbol{a} \tag{15.19}$$

$$C\boldsymbol{a}^+ (\tilde{E} - \tilde{H}_0)^{-1} \boldsymbol{a} + bC = \tilde{E}C \tag{15.20}$$

$$\tilde{E} = b + \sum_{k=1}^{N} \frac{a_k^2}{\tilde{E} - \tilde{E}_k^0} \tag{15.21}$$

We have equation of the type: $\tilde{E} = f(\tilde{E})$. We can solve it graphically: plot $y = \tilde{E}$ and $y = f(\tilde{E})$, and points where these two graphs cross are our solutions.

PICTURE HERE

As a result, we have estimations:

$$\tilde{E}_k \leq \tilde{E}_k^0 \tag{15.22}$$

which we wanted to prove — that expansion of the basis makes our estimations for excited states better.

Now we have to prove that $E_k \leq \tilde{E}_k$. How to do that? Let us start from the exact solution, and then will decrease size of the space. With previous result by induction we prove $E_k \leq \tilde{E}_k$.

This is important result showing that in principle we can describe excited states by a general CI model. However, practically, truncated CI models are not very accurate, and later we'll see why. We shall see that often larger linear subspaces would yield poorer approximations to transition energies! Moreover, what if in our subspace there is no vectors which can represent certain states??? For example, if for C$_{2v}$ molecule, we take A_1 determinants only, then we will not even know that other excited states exist. Likewise, at the CIS level, we remain blissfully unaware of doubly excited states!

Theorem 3

Now we shall consider so called minimax theorem, which does not require orthogonality to the exact ground state. It is though applicable to the linear spaces.

Minimax theorem says that if we consider variational estimation of the $k-th$ state of the Hamiltonian defined by:

$$\tilde{E}_k = min_\psi \frac{<\psi|H|\psi>}{<\psi|\psi>} \tag{15.23}$$

$$<\phi_i|\psi>= 0, \quad i = 1, \dots, k-1 \tag{15.24}$$

where $\{\phi_i\}$ are $k-1$ lowest *exact* eigenvalues of the Hamiltonian, the $\tilde{E}_k$ can be found from the following condition:

$$\tilde{E}_k = max_{\tilde{\phi}_i} min_\psi \frac{<\psi|H|\psi>}{<\psi|\psi>} \tag{15.25}$$

$$<\tilde{\phi}_i|\psi>= 0, \quad i = 1, \dots, k-1 \tag{15.26}$$

where $\tilde{\phi}_i$ are $k-1$ some arbitrary functions.

This means that: (i) we first fix $\{\tilde{\phi}_i\}$ and find minimum of $E = \frac{<\psi|H|\psi>}{<\psi|\psi>}$ with satisfying orthonormality condition $<\tilde{\phi}_i|\psi>= 0$; (ii) this $E = E[\{\tilde{\phi}_i\}]$ — is a functional of $\{\tilde{\phi}_i\}$. To find $\tilde{E}_k$, we have to find maximum of $E[\{\tilde{\phi}_i\}]$ by varying all $\{\tilde{\phi}_i\}$.

Proof: The dimensionality of the subspace defined by $\{\tilde{\phi}_i\}$ is $k-1$. Therefore if we consider k trial functions $\{\psi_i\}$, we can find at least one linear combination orthogonal to the subspace defined by $\{\tilde{\phi}_i\}$. The energy of this function is:

$$E = \frac{< \psi|H|\psi >}{< \psi|\psi >} = \frac{\sum_{l=1}^{k} |c_l|^2 E'_l}{\sum_{l=1}^{k} |c_l|^2} \leq E'_k \tag{15.27}$$

Thus, it always lower that E'_k and equality can be achieved by finding maximum of all minima. On the other hand, setting $k-1$ $\{\tilde{\phi}_i\}$ equal to exact $k-1$ lowest eigenstates of H, we achieve equality.

15.2 MCSCF models for excited states

Because of the limitations of CIS (lack of non-dynamical correlation and ability to describe doubly-excited electronic states), MCSCF methods are considered to be the best today.

Ground state MCSCF wavefunction:

$$\Psi = \sum_L C_L \Phi_L, \tag{15.28}$$

where L is usually small, and configurations are selected based on physical considerations. In MCSCF approach both coefficients C_L and orbitals are varied t optimize total energy of MCSCF wavefunction.

How can we describe excited states by MCSCF approach?

Option 1: Take similar anzats, $\Psi^* = \sum_{L^*} C_{L^*} \Phi_{L^*}$, and optimize energy (find best orbitals and best coefficients for this wavefunction). Problems:

- We will face same problems as with HF approximation: variational collapse to the ground state when states are not orthogonal by symmetry/spin-symmetry.
- Such approach will result in different set of orbitals for each of the states (e.g., group and excited). Non-orthogonal orbitals complicate significantly calculation of matrix elements between different states (e.g., transition dipole moments, non-adiabatic and spin-orbit couplings).
- Such approach suffers from arbitrariness in configuration selection. This problem becomes even more complicated than for ground state. Reasons: (i) While for the ground state valence configurations are of the major importance, excited states often involve mixing with non-valence configurations, e.g., Rydberg states. Besides, balanced description of two different states becomes merely impossible.

Option 2: Solve the problem for ground state. Describe excited states as higher CI roots. Not very good – since orbitals are optimized for ground state, hence, ground state is described much better than excited states. Non-balanced description introduces large errors into transition energies.

Option 3: State-averaged procedure. Consider ground state and excited state functions written as:

$$\Psi = \sum_L C_L \Phi_L \tag{15.29}$$

$$\Psi^* = \sum_{L^*} C_{L^*} \Phi_{L^*} \tag{15.30}$$

use the same set of orbitals for both states. Minimize averaged energy of both states:

$$E = n_0 E_0 + n^* E^* = n_0 < \Psi|H|\Psi > + n^* E^* < \Psi^*|H|\Psi^* >, \tag{15.31}$$

where n_0, n^* some arbitrary weights.

Both states are described equally poorly — neither of them is completely happy with the orbitals. However, we do not have problems with non-orthogonal orbitals and when states intersects.

Option 4: Describe excited state wavefunction by single excitations from the MCSCF wavefunction. This is generalization of CIS model, which is possible due to the variational nature of MCSCF wavefunction. Here we use generalized Brillouin theorem. This is most rigorous way to define excited states on top of MCSCF wavefunction. However, it assumes that orbital relaxation is small for excited states, which is not always the case. Such models (MCLR) were tested, and found to be not very efficient.

Accurate theories: MCSCF corrected for dynamical correlation: CASPT2, etc.

15.3 Linear Response Formalism for Ground and Excited States

15.3.1 Time-dependent variational principles

Frenkel time-dependent variational principle:

$$< \delta\Phi|H + V(t) - i\frac{\partial}{\partial t}|\Phi >= 0 \tag{15.32}$$

Explain meaning of this principle. In linear parameterizations — result is CI. In non-linear parameterizations — more complicated.

15.3.2 Linear response

For non-variational methods can replace variation $\delta\Phi$ to some other subspace.

Our starting point is time-dependent Schrödinger equation:

$$(H + \lambda V(t))|\Psi(t) >= i\frac{\partial}{\partial t}|\Psi(t) > \tag{15.33}$$

Since we do not know exact solution of the problem with time-independent Hamiltonian H, we cannot apply standard time-dependent perturbation theory approach for the whole problem (15.33). Instead, we shall seek for the solution of Eq(15.33) in the given finite subspace Ω defined by the some basis functions $\{\Phi_L\}_{L=1}^{N}$. To find a solution of Eq(15.33) in the subspace Ω we have to satisfy the following set of coupled equations:

$$< \Phi_L| \left((H + \lambda V(t)) - i\frac{\partial}{\partial t} \right) |\Psi(t) >= 0, \qquad L = 1, \ldots, N \tag{15.34}$$

We shall solve projective equations (15.34) by means of perturbation theory. Zero-order solution ($\lambda = 0$) shall define ground state energy and wavefunction. Poles of first order response equation will define resonances of ground state wavefunction, which correspond to excitation energies. Since resonance conditions in first order equations must be satisfied at any perturbation V, hence, we must satisfy them for $V = 0$ as well. This means that we do not need to know what is an perturbation V. However, we can use some information about time-dependence of V in order to guess about functional form of $|\Psi(t) >$. In other words, explicit form of V helps us to pick up a correct anzats for $|\Psi(t) >$.

15.3.3 CIS by linear response

Let us apply the linear response formalism to the Hartree-Fock wavefunction. Let us remember, that linear response will give us ground state and excited states energies.

To proceed with the derivation, we have to decide about basis $|\Phi_L >$ (many electron basis) we will use. The basis is defined by the space in which wavefunction is defined. Where HF wavefunction is defined? In a space of a single determinant? Yes, $E_{HF} =< \Phi_0|H|\Phi_0 >$. Is that all? No, HF wavefunction is defined in a space of single excitations as well:

$$F\phi_i = \epsilon_i\phi_i \tag{15.35}$$

$$< \Phi_i^a|H|\Phi_0 >= 0 \tag{15.36}$$

These are two equivalent forms of Hartree-Fock equations. First equation is what we derived, second equation is Brillouin theorem, an equivalent form of Hartree-Fock equations. The second equation shows that HF wavefunction is defined in a space of reference determinant and single excitations (VP results in the fact that single excitations do not mix with the HF reference).

We, hence, start from the following set of equations:

$$< \Phi_L| \left(H - i\frac{\partial}{\partial t} \right) |\Psi(t) >=< \Phi_L|\lambda V(t)|\Psi(t) >, \qquad \Phi_L = \{\Phi_0, \Phi_i^a\} \tag{15.37}$$

Wavefunction is given:

$$\Psi(t) = \Phi_0 e^{-iE_0 t} + \lambda T_1 \Phi_0 e^{-iE_1 t} \tag{15.38}$$

, where Φ_0 is time-independent Slater determinant, E_0 is energy of the ground state, and E_1 is an energy of the excited state. Here we use “frozen-orbitals” approximation

— we do not introduce time-dependence into the molecular orbitals, only into the amplitudes/phase of the wavefunction. For zero-order (λ^0) we have:

$$\Psi^{(0)}(t) = \Phi_0 e^{-iE_0 t} \tag{15.39}$$

$$< \Phi_L|(H - i\frac{\partial}{\partial t})|\Phi_0 e^{-iE_0 t} >= 0 \tag{15.40}$$

which gives:

$$< \Phi_L|H|\Phi_0 > e^{-iE_0 t} - E_0 < \Phi_L|\Phi_0 > e^{-iE_0 t} = 0 \tag{15.41}$$

$$< \Phi_L|H|\Phi_0 >= E_0 < \Phi_L|\Phi_0 > \tag{15.42}$$

$$< \Phi_0|H|\Phi_0 >= E_0 \tag{15.43}$$

$$< \Phi_i^a|H|\Phi_0 >= 0 \tag{15.44}$$

$$\tag{15.45}$$

These are Hartree-Fock equations! Now consider first order (λ^1):

$$\Psi^{(1)}(t) = T_1 \Phi_0 e^{-iE_1 t} \tag{15.46}$$

$$< \Phi_L|(H - i\frac{\partial}{\partial t})|T_1 \Phi_0 e^{-iE_1 t} >=< \Phi_L|V(t)|T_1 \Phi_0 e^{-iE_1 t} > \tag{15.47}$$

$$\tag{15.48}$$

Since we seek for the resonance conditions, we have to satisfy the equation for any V, including $V = 0$. Hence,

$$< \Phi_L|(H - i\frac{\partial}{\partial t})|T_1 \Phi_0 e^{-iE_1 t} >= 0 \tag{15.49}$$

$$< \Phi_L|H|T_1 \Phi_0 > e^{-iE_1 t} - E_1 < \Phi_L|T_1 \Phi_0 > e^{-iE_1 t} = 0 \tag{15.50}$$

$$< \Phi_L|H|T_1 \Phi_0 >= E_1 < \Phi_L|T_1 \Phi_0 > \tag{15.51}$$

$$< \Phi_0|H|T_1 \Phi_0 >= 0 \tag{15.52}$$

$$< \Phi_i^a|H|T_1 \Phi_0 >= E_1 t_i^a \tag{15.53}$$

$$\tag{15.54}$$

These are CIS equations!

15.3.4 EOM-CC: Excitation energies for the CC wavefunctions by linear response theory. CCD example

Let us start from the general definition of the time-dependent coupled-cluster wavefunction

$$|\Psi(t) >= e^{T(t)}|\Phi_0 > e^{-iE(\lambda,t)} \tag{15.55}$$

We introduce no time-dependence into $|\Phi_0 >$ using frozen orbitals approximation. We will truncate operator T by including only single and double excitations. For ground state we will retain only double excitations (CCD model).

$$T(t) = T_2 + \lambda U_1(t) + \lambda U_2(t) \tag{15.56}$$

For the sake of simplicity we make an assumption about form of the perturbation V:

$$\lambda V(t) = \lambda \hat{\mu}(e^{i\omega t} + e^{-i\omega t}) \tag{15.57}$$

Form of perturbation Eq.(15.57) defines time-dependence in a wavefunction amplitudes in first-order response equations: time-dependence of amplitudes in linear response follows time-dependence of perturbation:

$$\begin{aligned} U_1(t) &= U_1 e^{-i\omega t} \\ U_2(t) &= U_2 e^{-i\omega t} \end{aligned} \tag{15.58}$$

The subspace Ω is defined by the truncation of operator T (15.56) in the wavefunction (15.55): reference Hartree-Fock determinant, all single and double excitations define a subspace for Eq.(15.34).

Zero-order solution of Eq(15.33) for CCD-wavefunction (15.55,15.56) yields equations defining projective Brueckner CCD energy and wavefunction:

$$E^{(0)} = E_{CCD} = < \Phi_0|H|(1+T_2)\Phi_0 > \tag{15.59}$$

$$< \Phi_i^a|H|(1+T_2)\Phi_0 >= 0 \tag{15.60}$$

$$< \Phi_{ij}^{ab}|H|(1+T_2+\frac{1}{2}T_2^2)\Phi_0 >= a_{ij}^{ab} E_{CCD} \tag{15.61}$$

Since our ground state model is not projective Brueckner CCD, the linear response equations for VBCCD can be different from equations below. For now, we will use linear response equations for projective BCCD model as they are.

First order response equations results in:

$$< \Phi_i^a|H|(U_1+U_2+U_1T_2)\Phi_0 >= u_i^a(E_{CCD}+\omega) \tag{15.62}$$

$$< \Phi_{ij}^{ab}|H|(U_1+U_2+U_1T_2+U_2T_2)\Phi_0 > -a_{ij}^{ab} < \Phi_0|H|(U_1+U_2)\Phi_0 >= u_{ij}^{ab}(E_{CCD}+\omega) \tag{15.63}$$

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