APPENDIX

APPENDIX A

Theoretical Background

The Theory of Quantum Chemical Calculations: Ground State Methods

Molecular orbital theory is concerned with predicting the properties of atomic and molecular systems. It is based upon the fundamental laws of quantum mechanics and uses a variety of mathematical transformation and approximation techniques to solve the fundamental equations, in contrast to semi-empirical models.

1. The Schrödinger Equation

The quantum chemical methods are based on finding solutions to the Schrödinger equation on molecular orbital theory. Quantum mechanics explains how entities like electrons have both particle-like and wave-like characteristics. The time independent Schrödinger equation for a molecule (n-electron and N-nuclei system):

$$H\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R}) \qquad (1)$$

and the Hamiltonian is (in atomic units):

$$H = T + V$$

$$H = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad (2)$$

where T and V are the kinetic and potential energy operators, respectively, which separate out the motion of the nuclei from the motion of the electrons, equation (2) can be rewritten as

$$H = -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + H_{el} \tag{3}$$

This focus on the electronic Hamiltonian, H_{el}, and try to solve the electronic Schrödinger equation in the field of the fixed nuclei. The nuclear-nuclear repulsion term (the final in equation (2)) appears as a constant in H_{el}. Further assume the wave function $\psi(\vec{r}, \vec{R})$ to be a product of an electronic and a nuclear part:

$$\psi(\vec{r}, \vec{R}) = \psi_{elec}(\vec{r}, \vec{R})\psi_{nucl}(\vec{R}) \tag{4}$$

The justification for this is that the electrons are much lighter than the nuclei. This is called the Born-Oppenheimer approximation. The parametric $\vec{R}$ dependence of ψ_{elec} arises since the electron distribution depends implicitly on the particular nuclear arrangement for the system under study. The nuclear wave function, ψ_{nucl}, describes the vibrational, rotational and translational motion of the nuclei. From (1), (3) and (4) can obtain;

$$H\psi(\vec{r}, \vec{R}) = H\psi_{elec}(\vec{r}, \vec{R})\psi_{nucl}(\vec{R}) = \left(-\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + H_{el} \right)\psi_{elec}(\vec{r}, \vec{R})\psi_{nucl}(\vec{R})$$

$$= \left(-\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + E_{el} \right)\psi_{elec}(\vec{r}, \vec{R})\psi_{nucl}(\vec{R}) = E\psi_{elec}(\vec{r}, \vec{R})\psi_{nucl}(\vec{R}) = E\psi \tag{5}$$

The electronic wavefunction $\psi_{elec}(\vec{r}, \vec{R})$ can be divided out from both sides of equation (5), provided that terms in $\nabla^2\psi_{elec}(\vec{r}, \vec{R})$ are small, i.e. the electronic wavefunction changes slowly upon small displacements of the nuclear positions. Thus, if we neglect the influence of the nuclear derivative on the electron wave function (ψ_{el}) (i.e. the nuclei move slowly compared with the electrons) which can separate equation (5) into two equations, an electronic part:

$$H_{el}\psi_{el}(\vec{r},\vec{R}) = E_{el}(\vec{R})\psi_{el}(\vec{r},\vec{R}) \tag{6}$$

where

$$H_{el} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \tag{7}$$

and a nuclear part:

$$H_{nucl}\psi_{nucl}(\vec{R}) = E\psi_{nucl}(\vec{R}) \tag{8}$$

where

$$H_{nucl} = -\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 + E_{el}(\vec{R}) \tag{9}$$

2. Hartree Fock Theory

An exact solution to the Schrödinger equation is not possible for any but the most trivial molecular systems. However, a number of simplifying assumptions and procedures do make an approximate solution possible for a large range of molecules. To simplify the treatment further, the next step is to assume that the electrons are non-interacting. This implies that (apart from the constant nuclear-nuclear repulsion term) which can rewrite the total n-electron Hamiltonian as a sum of n one-electron Hamiltonians,

$$H_{el} = \sum_{i=1}^{N} h(i) \tag{10}$$

$$h(i) = \left(-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}}\right) \tag{11}$$

This is clearly an oversimplification, since have neglected the electron-electron repulsion term $\frac{1}{r_{ij}}$. Equation (10) defines the independent particle model. The one-electron Hamiltonians (equation (11)) are termed core-Hamiltonians, since the only interactions included are those between the electrons and the bare nuclei. Including an average interaction term in the $\{h(i)\}$, these become effective one-electron Hamiltonians. As a consequence of equation (10), the total wave function can be rewritten as a product of n single-particle wave functions,

$$\psi(\vec{r}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\ldots\phi_n(\vec{r}_n) \tag{12}$$

or, take the electron spin into account,

$$\psi = \chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\ldots\chi_n(\vec{x}_n) \tag{13}$$

The spin orbitals $\{\chi_i(\vec{x}_i)\}$ are the products of the spatial orbitals $\phi_i(\vec{r}_i)$ and the spin functions ($\alpha(\omega)$ and $\beta(\omega)$); $\vec{x}_i$ denotes both the space and spin coordinates of electron i. The total independent particle spin-orbital wave function (equation (13)) is called a Hartree-product. This is an eigenfunction of the n-electron model Hamiltonian defined in equation (10), and the corresponding eigenvalue is a sum of the single-particle spin-orbital energies,

$$E_{el} = \sum_{i=1}^{M} \varepsilon_i \tag{14}$$

A further requirement on the state wave function (13) is that it must be anti-symmetric with respect to the interchange of coordinate r (both space and spin) of any two electrons,

$$\left|\psi(\vec{x}_1, \vec{x}_{2,\ldots,} \vec{x}_n)\right|^2 = \left|\psi(\vec{x}_2, \vec{x}_1, \ldots, \vec{x}_n)\right|^2 \tag{15}$$

$$\psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) = \pm\psi(\vec{x}_2, \vec{x}_1, \ldots, \vec{x}_n) \tag{16}$$

It is also possible to write equation (16) in terms of a $n \times n$ determinant, a Slater determinant, which has the same antisymmetric properties:

$$\psi = (n!)^{-1/2} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_n(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & & \\ \cdots & & \cdots & \\ \chi_1(\vec{x}_n) & \chi_2(\vec{x}_n) & \cdots & \chi_n(\vec{x}_n) \end{vmatrix} \tag{17}$$

Which commonly is written like:

$$|\psi\rangle = (n!)^{-1/2} |\chi_1(\vec{x}_1), \chi_2(\vec{x}_2), \ldots, \chi_n(\vec{x}_n)\rangle \tag{18}$$

It can easily be verified that the Slater determinant obeys the Pauli principle, as the determinant then becomes zero. The pre-factor $(n!)^{-1/2}$ is a normalisation constant, and the $\{\chi_i\}$ are assumed orthonormal. By antisym-metrizing the Hartree-product (13) in the form of a Slater determinant (17), that the probability of finding any two electrons at the same point in space (i.e. $\vec{x}_1 = \vec{x}_2$) is zero.

Through the wave functions, the effective potential is generated. This potential allows refining wave functions, from which a new potential is obtained. The procedure is repeated until a stable, self-consistent solution is reached. Due to the iterative procedure, the initial guess of the wave function can of course be chosen ad hoc. However, the better the initial guess is, the easier it is to reach a stable solution to the eigenvalue problems in a relatively short computational time, is provided by the variation principle. This can be stated in the following way: Given any approximate wave function, satisfying the correct boundary conditions, the expectation value of the energy obtained by this wave function never lies below the exact energy of the ground state. Expressed in mathematical terms:

$$E_e = \frac{\langle \psi | H_e | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_{exact} \tag{19}$$

A conceptually appealing model for the (trial) wave function of our molecular system is to regard it as being constructed from molecular orbitals (MO). This description in analogous to the model used for the atomic orbitals (AO). The MO's, the elements of the wave function determinant, are in turn thought of as being constructed by a Linear Combination of Atomic Orbitals (LCAO),

$$\psi_i^{MO} = \sum_{\mu} c_{\mu i} \phi_{\mu}^{AO} \tag{20}$$

The variational principle leads to following equations describing the molecular orbital expansion coefficients, $c_{\nu i}$, derived by Roothaan and by Hall:

$$\sum_{\nu=1}^{N} \left(F_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) c_{\nu i} = 0 \quad \mu = 1,2,\ldots, N \tag{21}$$

Equation 21 can be rewritten in matrix form:

$$FC = SC\varepsilon \tag{22}$$

with

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\lambda|\nu\sigma) \right] \tag{23}$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} + G_{\mu\nu} \tag{24}$$

where $H_{\mu\nu}^{core}$, core-Hamiltonian matrix, defined as

$$H_{\mu\nu}^{core} = \int dr_1 \phi_{\mu}^{*}(1) h(1) \phi_{\nu}(1) \tag{25}$$

The matrix P is the density matrix or charge- and bond-order matrix,

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*} \qquad (26)$$

The matrix S is the overlap matrix, indicating the overlap between orbitals.

$$S_{\mu\nu} = \int dr_1 \phi_{\mu}^{*}(1)\phi_{\nu}(1) \qquad (27)$$

The term $(\mu\nu|\lambda\sigma)$ in Equation 23 signified the two-electron repulsion integrals, defined as

$$(\mu\nu|\lambda\sigma) = \int dr_1 dr_2 \phi_{\mu}^{*}(1)\phi_{\nu}(1) r_{12}^{-1} \phi_{\lambda}^{*}(2)\phi_{\sigma}(2) \qquad (28)$$

The (initial) wave function is used to generate an effective potential, which apply this potential in order to refine the coefficient matrix. The modified MO's form the new input in the Roothaan equations, and a new potential is generated. The iterative procedure is repeated until convergence is reached, i.e. when the changes in energy and/or charge density in two subsequent iterations are below a pre-set threshold value.

Before a more technical description of the SCF-procedure is presented, first need to define a new transformation matrix X, used for orthogonalisation of the basis set. This orthogonalisation can be either symmetric or canonical. A symmetric orthogonalisation implies that X is formed through the relation

$$X = S^{-1/2} = Us^{-1/2}U^{\tau} \qquad (29)$$

where S is the overlap matrix, U is an unitary matrix which diagonalizes S, and the diagonal matrix of the eigenvalues of S is given by the relations. In the canonical orthogonalisation procedure, X is instead given by

$$X = Us^{-1/2} \tag{30}$$

Consider a new coefficient matrix C' related to the old coefficient matrix C by

$$C' = X^{-1}C, \qquad C = XC' \tag{31}$$

where assumed that X possesses an inverse. Substituting $C = XC'$ into the Roothaan equations gives

$$FXC' = SXC'\varepsilon \tag{32}$$

Multiplying on the left by X^{τ} gives

$$\left(X^{\tau}FX\right)C' = \left(X^{\tau}SX\right)C'\varepsilon \tag{33}$$

if define a new matrix F^{τ} by

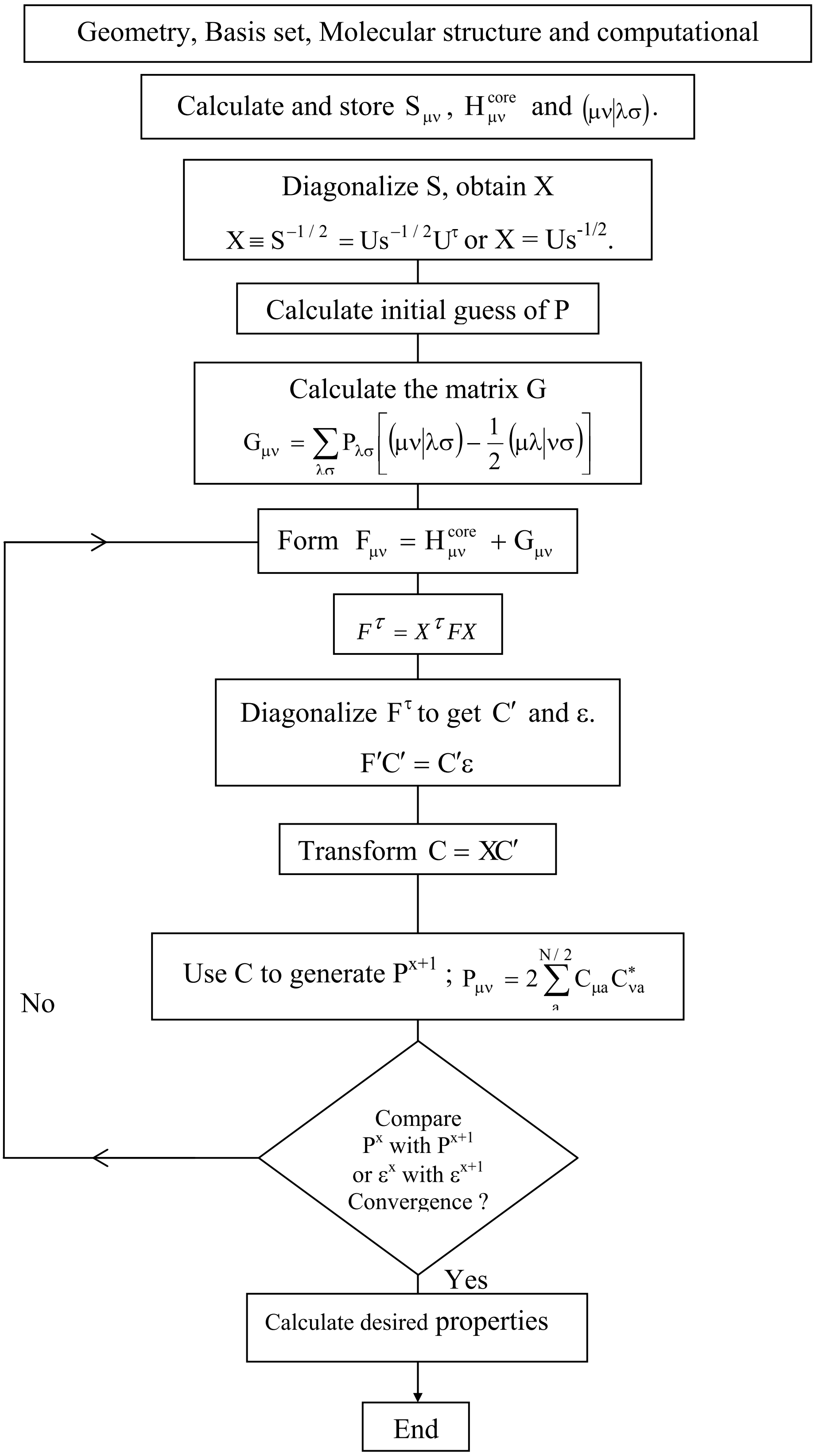
$$F^{\tau} = X^{\tau}FX \tag{34}$$

and use (27),then

$$F'C' = C'\varepsilon \tag{35}$$

The SCF procedure, outlined in Appendix figure A1, is as follows

1. Specify a molecule (a set of nuclear coordinates $\{R_A\}$, atomic numbers $\{Z_A\}$, and number of electron N) and a basis set $\{\phi_\mu\}$.
2. Calculate all required molecular integrals, $S_{\mu\nu}$, $H_{\mu\nu}^{core}$ and $(\mu\nu|\lambda\sigma)$.
3. Diagonalize the overlap matrix S and obtain a transformation matrix X from either equation $X \equiv S^{-1/2} = Us^{-1/2}U^\tau$ or $X = Us^{-1/2}$.
4. Obtain a guess at the density matrix P.
5. Calculate the matrix G of equation $F_{\mu\nu} = H_{\mu\nu}^{core} + G_{\mu\nu}$ from the density matrix P and the two-electron integral $(\mu\nu|\lambda\sigma)$.
6. Add G to the core-Hamiltonian to obtain the Fock matrix $F = H^{core} + G$.
7. Calculate the transformed Fork matrix $F^\tau = X^\tau FX$
8. Diagonalize F^τ to obtain C' and ε.
9. Calculate $C = XC'$.
10. Form a new density matrix P from C using $P_{\mu\nu} = 2\sum_a^{N/2} C_{\mu a}C_{\nu a}^*$.
11. Determine whether the procedure has converged, i.e. determine whether the new density matrix of step (10) is the same as the previous density matrix within a specified criterion. If the procedure has not converged, return to step (5) with the new density matrix.
12. If the procedure has converged, then use the resultant solution, represented by C, P, F, etc., to calculate expectation values and other quantities of interest.



Appendix Figure A1 Schematic view of a Hartree-Fock self consistent field calculation.

3. Basis Set

The basis set most commonly used in quantum mechanical calculations are composed of atomic functions. The next approximation involves expressing the molecular orbitals as linear combinations of a pre-defined set of one-electron functions known as basis function. An individual molecular orbitals is defined as:

$$\phi_i = \sum_{\mu=1}^{N} c_{\mu i}\chi_\mu \tag{36}$$

where the coefficients $c_{\mu i}$ are known as molecular orbital expansion coefficients. The basis function $\chi_1 ... \chi_N$ are also chosen to be normalized. Gaussian-type atomic functions were used as basis functions. Gaussian functions have the general form

$$g(\alpha, \vec{r}) = cx^n y^m z^l e^{-\alpha r^2} \tag{37}$$

where $\vec{r}$ is of course composed of x, y, and z. α is a constant determining the size (radical extent) of the function. In Gaussian function, $e^{-\alpha r^2}$ is multiplied by powers (possibly 0) of x, y, and z and a constant for normalization, so that:

$$\int_{\text{allspace}} g^2 = 1 \tag{38}$$

Thus, c depends on α, l, m, and n.

Here are three representative Gaussian functional (s, p_y and d_{xy} types, respectively):

$$g_s(\alpha, \vec{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

$$g_y(\alpha, \vec{r}) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} ye^{-\alpha r^2}$$

$$g_{xy}(\alpha, \vec{r}) = \left(\frac{2048\alpha^7}{\pi^3}\right)^{1/4} xye^{-\alpha r^2} \tag{39}$$

Linear combinations of primitive gaussians like these are used to form the actual basis functions; the latter are called contracted Gaussians and have the form

$$\chi_\mu = \sum_P d_{\mu p} g_p \tag{40}$$

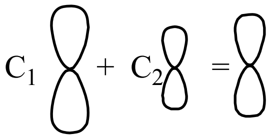
where the $d_{\mu p}$'s are fixed constants within a given basis set. Note that contracted functions are also normalized in common practice. A few commonly used basis sets are lists as following.

Minimal Basis Sets: Minimal basis sets contain the minimum number of basis functions needed for each atom, as in these examples:

H: 1s
C: 1s, 2s, $2p_x$, $2p_y$, $2p_z$

Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set is a minimal basis set (although it is not the smallest possible basis set). It used three gaussian primitives per basis function, which accounts for the “3G” in its name. “STO” stands for “Slater-type orbitals,” and the STO-3G basis set approximates Slater orbitals with gaussian functions.

Split Valence Basis Sets



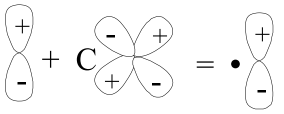
The first way that a basis set can be made larger is to increase the number of basis functions per atom. Split valence basis sets, such as 3-21G and 6-31G, have two (or more) sized of basis function for each valence orbital. For example, hydrogen and carbon are represented as:

H: 1s, 1s'
C: 1s, 2s, 2s', $2p_x$, $2p_y$, $2p_z$, $2p'_x$, $2p'_y$, $2p'_z$

where the primed and unprimed otbitals differ in size.

The double zeta basis sets, such as the Dunning-Huzinaga basis set (D95), form all molecular orbitals from linear combinations of two sized of functions for each atomic orbital. Similarly, triple split valence basis sets, like 6-311G, use three sizes of contracted functions for each orbital-type.

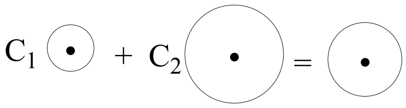
Polarized Basis Sets



Split valence basis sets allow orbitals to change size, but not to change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example, polarized basis sets add d functions to carbon atoms and f functions to transition metals, and some of them add p functions to hydrogen atoms.

So far, the only polarized basis set 6-31G(d) is used. Its name indicates that it is the 6-31G basis set with d functions added to heavy atoms. This basis set is becoming very common for calculations involving up to medium-sized systems. This basis set is also known as 6-31G*. Another popular polarized basis set is 6-31G(d,p), also known as 6-31G**, which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms.

Diffuse Functions



Diffuse functions are large-size versions of s- and p- type functions (as opposed to the standard valence-size functions) which allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, descriptions of absolute acidities. The 6-31+G(d) basis set is the 6-31G(d) basis set with diffuse functions added to heavy atoms. The double plus version, 6-31++G(d), adds diffuse functions to the hydrogen atoms as well. Diffuse functions on hydrogen atoms seldom make a significant difference in accuracy.

High Angular Momentum Basis Sets

Even larger basis sets are now practical for many systems. Such basis sets add multiple polarization functions per atom to triple zeta basis set. For example, the 6-31G(2d) basis set adds two d functions per heavy atom instead of just one, while the 6-311++G(3df,3pd) basis set contains three sets of valence region functions, diffuse functions on both heavy atoms and hydrogens, and multiple polarization funtions:3 d functions and 1 f function on heavy atoms and 3 p functions and 1 d function on hydrogen atoms. Such basis sets are useful for describing the interactions between electrons in electron correlation methods.

4. Density Functional Theory

Methods that are rooted in the so-called density functional theory are currently regarded as very promising since are able to include a large amount of correlation effects in a formalism that essentially requires very similar computational resources as the Hartree-Fock procedure. In fact the algorithms of the approach, in which the electron density is described in terms of one-electron basis functions, are very similar to the single-determinant HF algorithm. This property has helped to establish density functional methods as a standard tool for chemistry and physics.

While the concept of expressing part or all of the molecular energy as a functional of the electron density goes back to the early days of quantum theory, Density Functional Theory (DFT) was put on a rigorous theoretical foundation by the Hohenberg-Kohn theorem. It states that there exists unique density ρ that yields the exact ground energy of system. The subsequent work of Kohn and Sham laid the basis for practical computational applications of the DFT to real systems. The basis of their formalism is the so-called Kohn-Sham equations.

$$H\Psi_i = E_i\Psi_i \tag{41}$$

in which the Hamiltonian H is defined as

$$H = \left(-\frac{1}{2}\nabla^2 + V_{KS} \right) \tag{42}$$

where V_{KS} is a local potential defined such that the total density of the non-interacting system

$$\rho = \sum_{i} |\Psi_i|^2 \tag{43}$$

is the same as the density of the “real” system. V_{KS} has the three components V_{ext}, V_C and V_{XC} containing the nuclear and external, Coulomb potential of the electrons and the exchange-correlation interactions.

$$E_{KS} = V_{ext} + \sum_{\mu v} P_{\mu v} H_{\mu v} + \frac{1}{2} \sum_{\mu v \lambda \sigma} P_{\mu v} P_{\lambda \sigma} \Im + E_x(P) + E_C(P) \tag{44}$$

In most cases the expressions for E_C and E_X cannot be computed analytically and must be obtained by numerical methods. The key difference between the Hartree-Fock and Kohn-Sham approaches to the SCF methods is the term E_{XC}, which was mostly omitted in above discussion. In HF theory, this E_{XC} is written as

$$E_{XC}^{HF} = \frac{1}{2} \sum_{\mu v \lambda \sigma} (P_{\mu v}^{\alpha} P_{\lambda \sigma}^{\alpha} P_{\mu v}^{\beta} P_{\lambda \sigma}^{\beta})(\mu v / \lambda \sigma) \tag{45}$$

while the KS theory introduces a functional

$$E_{XC}^{HF} = \int f(\rho^{\alpha}, \rho^{\beta}, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}) dr \tag{46}$$

for the description. The density gradient invariants γ ($\gamma_{xy} = \nabla \rho_x \nabla \rho_y$)

Density Functionals

It is often customary to make a partition of the density functional into an exchange and correlation part for the separation of

$$E_{XC}(\rho) = E_X(\rho) + E_C(\rho) \tag{47}$$

Although distinction between exchange and correlation contributions is somewhat artificial in the context of DFT, the above separation considerably simplifies the discussion. It should, however, be explicitly noted that the definition of E_C does not correspond to the *ab initio* E_C since correlation has, by definition, meaning only in a mean field approximation and DFT is not using such an approximation. The exchange part, on the other hand, follows closely the HF definition of exchange, does however not necessarily reproduce the exact exchange.

Exchange

The exchange energy of a uniform spin-polarized gas of spin density ρ_σ is

$$E_X^S = -\sum \int \rho^\sigma(r) f_X^S(\rho_\sigma(r))dr \tag{48}$$

with $f_X^S(\rho_\sigma(r)) = \alpha_X[\rho_\sigma(r)]^{\frac{1}{3}}$ and $\alpha_X = \frac{3}{2}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}$. The exchange expression is sometimes labeled *Slater exchange*, thus the superscript *S*. This exchange expression serves as a base for other functional, which can be conveniently expressed in terms of their enhancement factor F_X over the exchange of the uniform electron gas

$$E_X = -\sum_\sigma \int \rho_\sigma(r) f_X^S(\rho_\sigma(r)) F_X(\rho_\sigma)(\gamma_{\sigma\sigma}(r))dr \tag{49}$$

For instance, the exchange functional proposed by Perdew and Wang uses the following factor:

$$F_X^{PW}(s) = \left[1 + 0.0864\frac{s^2}{m} + bs^4 + cs^6\right]^m \tag{50}$$

with $m = 1/15$, $b = 14$, $c = 0.2$ and $s = (24\pi^2)^{-1/3}\sqrt{(\gamma_{\sigma\sigma}/\rho^{4/3})}$ $\gamma_{\sigma\sigma}$ here is again the squared density gradient ∇_ω^2. One of the most used exchange functionals is that of Becke 1988, which is often labeled B88 or simply B.

$$F_x^B = -\beta\rho^{1/3}\frac{x^2}{1+6\beta\sinh^{-1}(x)} \tag{51}$$

which uses the values $x = \sqrt{(\gamma_{\sigma\sigma}/\rho_\sigma^{4/3})}$ and $\beta = 0.0042$ in order to maintain correct boundary conditions. In a different approach, Perdew and Wang proposed an exchange formula that is designed from purely first principles.

$$F_X^{PW91} = \frac{1+(a_1 s)(a_2 s)\sinh^{-1}+(a_3+a_4\exp(-100s^2))s^2}{1+(a_1 s)(a_2 s)\sinh^{-1}+a_5 s^4} \tag{52}$$

where $a_1 = 0.19645$, $a_2 = 7.7956$, $a_3 = 0.2743$, $a_4 = -0.1508$, $a_5 = 0.004$ and s the same as in eq. 50.

In practice, the three above exchange functionalism are very similar, and are in fact based on minor corrections to the previous ones. Therefore they can be expected to produce very similar results. The enhancements over the simple electron gas, however, are significant enough and usually constitute a major improvement.

Correlation

While it is possible to obtain E_C by some numerical methods from E_{XC} and the already known EX (cf. eq. 47) for the uniform electron gas, it is much more common to use separate correlation functionals. Distinction is made between local and gradient corrected functionals, referring to absence or presence of first order terms of the density ρ_σ. The local functional proposed by Vosko, Wilk and Nusair (VWN) was obtained using Pad's approximated interpolations of Ceperley and Alder results of their accurate quantum Monte Carlo calculations for the homogeneous electron gas. The functional is,

$$E_C^{VWN} = \frac{A}{2}\left[\ln\frac{x^2}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b} - \frac{bx_0}{X(x_0)}\left(\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{(2x+b)}\right)\right] \quad (53)$$

where the functions $x = r_b^{1/2}$, $X(x) = x^2 + bx + c$ and $Q = (4c - b^2)^{1/2}$ and the constants are $A = 0.0621814$, $x_0 = -0.409286$, $b = 13.0720$ and $c = 42.7189$. r_b represents are the Wigner-radius and is defined by $1/\rho = \frac{4\pi}{3}(r_b)^3$. Together with the exchange expression from eq. 48 this constitutes what is often called the local density approximation (LDA) or local spin density approximation (LSDA) when spin is considered.

Due to the experiences with the LDA and as a consequence of some of its shortcomings, recent developments have resulted in a number of gradient corrections to local functionals like the aforementioned VWN or a completely new class of gradient corrected functionals.

Another frequently used functional has been published by Lee, Yang and Parr. It replaces both the local and the gradient part of the LDA correlation functional.

$$E_C^{LYP} = -a\frac{1}{1+d\rho^{-1/3}}\left\{\rho + b\rho^{-2/3}\left[C_F\rho^{-5/3} - 2t_w + \frac{1}{9}\left(t_w + \frac{1}{2}\nabla^2\rho\right)\right]e^{-2c\rho^{-1/3}}\right\} \quad (54)$$

where $t_w = \frac{1}{8}\left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2\rho\right)$ and $C_F = \frac{3}{10}(3\pi^2)^{2/3}$, $a = 0.04918$, $b = 0.132$, $c = 0.2533$ and $d = 0.349$

Hybrid Functionals

More recently, following an approach proposed by Becke, the combination of DFT functionals with *ab initio* formulations led to a class of expressions which are essentially a mixture of both DFT and HF contributions with fitted coefficients for each contribution. The aim of this approach is to provide expressions that include the full exchange contribution and avoid side-effects arising from a complete replacement of the DFT exchange expression by the HF one. As an example, the B3LYP functional looks like this:

$$E_{XC}^{B3LYP} = a_{X0}E_X^S + (1-a_{X0})E_X^{HF} + a_{X1}\Delta E_X^B + E_C^{VWN} + a_C\Delta E_C^{LYP} \qquad (55)$$

with $a_{X0} = 0.80$, $a_{X1} = 0.72$ and $a_C = 0.81$, which are values fitted for a selected set of molecules to reproduce the heat of formation. The term E_X^{HF} is calculated using the Kohn-Sham orbitals in the manner of the HF procedure by computing the exchange integrals $(\mu v / v\mu)$. The B3LYP functional often uses $\Delta E_C^{3LYP} = E_C^{LYP} - E_C^{VWN}$.

The Theory of Quantum Chemical Calculations: Excited State Methods

1. Excited Slater Determinants

The Hartree-Fock method generates solutions to the Schrodinger equation where the real electron-electron interaction is replaced by an average interaction. In the sufficiently large basis, the HF wave function is able to account for ~ 99% of the total energy, but the remaining ~1% is often very important for describing chemical phenomena. It is therefore clear that in order to improve on HF results, the starting point must be a trial wave function which contains more than one Slater Determinant (SD) Φ. Then electron correlation methods normally use the HF wave function as a starting point for improvements.

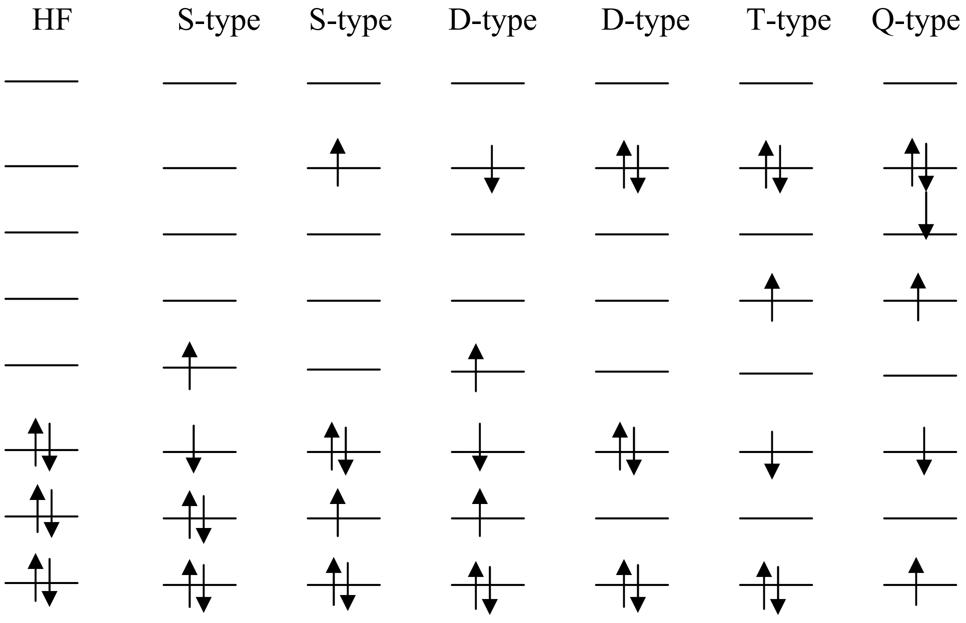
A generic multi-determinant trial wave function can be written as

$$\Psi = a_0\Phi_{HF} + \sum_{i=1} a_i \Phi_I \qquad (56)$$

where a_0 usually is close to 1. Electron correlation methods differ in how they calculate the coefficients in front of the other determinants, a_0 being determined by the normalization condition.

How are the additional determinants beyond the HF constructed? With *N* electrons and *M* basis functions, solution of the Roothaan-Hall equations for the RHF case will yield *N/2* occupied MOs and *M – N/2* unoccupied (virtual) MOs. A slater determined by *N/2* spatial MOs multiplied by two spin functions to yield *N* spinorbitals. By replacing MOs which are occupied in the HF determinant by MOs which are unoccupied, a whole series of determinants may be generated as shown in Figure A2. These can be denoted according to how many occupied HF MOs have been replaced by unoccupied MOs, i.e. Slater determinants which are *singly, doubly, triply, quadruply* etc. excited relative to the HF determinants, up to a maximum of *N* excited electrons. These determinants are often referred to as *Singles* (S), *Doubles* (D), *Triples* (T), *Quadruples* (Q) etc.

The total number of determinants that can be generated depends on the size of the basis set, the larger the basis, the more virtual MOs, and the more excited determinants can be constructed. If all possible determinants in a given basis set are included, all the electron correlation (in the given basis) is (or can be) recovered. Methods which include electron correlation are thus two-dimensional, the larger the one-electron expansion (basis set size) and the larger the many-electron expansion (number of determinants), the better are the results.



Appendix Figure A2 Excited Slater determinants generated from a HF reference.

2. Molecular Orbital Theories for Excited States

2.1 Configuration Interaction (CI)

The term “configuration” was originally used for the interaction of just a few Slater determinants required for the proper description of some electronic states of atoms and molecules, though the concept of configuration interaction has been known as a tool for obtaining, at least in principle, the exact solution of the Schrodinger equation since the early days of quantum mechanics. The results of CI calculations, and especially the results of full configuration (FCI) calculations, have been used as benchmarks for testing the newly developed methods. FCI is still the only method which is used for the definition of the correlation energy as the difference between the exact nonrelativistic energy (represented by the FCI energy) and the Hartree-Fock (HF) energy:

$$E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}} \qquad (57)$$

CI is still a standard method for calculation of excited electronic states and its conceptual simplicity makes it the method of choice for qualitative explanation of phenomena for which the single-determinant Hartree-Fock approximation is unsatisfactory because of near-degeneracies or rearrangement of electrons within partly occupied shells.

Definition and the essence of configuration interaction

For any CI calculation, we need first an orbital set, i.e., a set of one-electron functions $\varphi = \{\varphi_i, i = 1, 2, \ldots, m\}$, that satisfy the orthonormality

$$\langle \varphi_i \mid \varphi_j \rangle = \delta_{ij} \qquad (58)$$

and the completeness conditions

$$\sum_i |\varphi_i\rangle \langle\varphi_i| = 1 \qquad (59)$$

In the most applications these orbitals are chosen to be Hartree-Fock orbitals, though as will be noted below other types of orbitals (Huckel orbitals, natural orbitals, or even nonorthogonal orbitals) may also be used.

Next the orbitals are in a certain order, for example in the order of their increasing energy. Then assign to each orbital φ_i an occupation number n_i , which may take the 0, 1, or 2. The sum of the occupation numbers must be equal to the number of electrons. A set of occupation numbers (n_1, n_2, …, n_m) is called a *configuration*. In the ground state configuration of a closed-shell system all the lowest orbitals are doubly occupied. For example, for a ten electron system and the orbital set with m = 7, the ground state configuration is (2222200). The configuration (2222110), corresponding to the excitation of a single electron from orbital 5 to orbital 6, is called a singly excited configuration.

For a configuration having *n* singly occupied orbitals, we can in general form 2^n spin functions and therefore also 2^n different Slater determinants. A true number of linearly independent spin functions for a given configuration, i.e., for an orbital product function, and a total spin *S* is given by following formula:

$$f(n, S) = \binom{n}{q} - \binom{n}{q-1} \qquad (60)$$

where

$$q = \tfrac{1}{2}n - S \qquad (61)$$

In general the selected functions are linear combinations of several Slater determinants and, in contrast to individual Slater determinants, they are eigenfunctions of the spin operators S_z and S^2. Therefore they are called spin-adapted configuration fuctions or, most frequently, *configuration state functions* (CSFs). The spin adapted reference configuration is called the reference state function. Because of orthogonality of orbitals and spin functions, the CSFs are also orthogonal, and because of the completeness of the orbital set, a set of all possible CSFs forms a complete set

$$\sum_i \mid \Phi_i> \ < \Phi_i \mid = 1 \qquad (62)$$

Hence the exact wave function for a particular orbitals set may be expressed as

$$\Psi = \sum_i \ \left|\Phi_i\right\rangle\left\langle\Phi_i\middle|\Psi\right\rangle \qquad (63)$$

where the overlab intergrals between CSFs and the exact wave function have the meaning of expansion coeffients.

$$\Psi = \sum_i \ C_i \, \Phi_i \qquad (64)$$

Use of a complete set of CSFs in the expansion (63) is referred to as the complete or full configuration (FCI). Since FCI calculations are computationally very demanding, they are only feasible for small sets and a small number of electrons. In chemical applications of the CI method, smaller expansions are used in order to develop a computationally tractable model. Standard levels of the CI method are termed according to the extent of the CI expansion: CIS, CISD, CISDT, and CISDTQ correspond to expansions through singly, doubly, triply and quadruply excited CSFs, respectively. Those methods will be called truncated CI methods. Truncating the excitation level at 1 (CI with Singles, CIS) does not give any improvement over the HF result as all matrix elements between the HF wave function and singly excited determinants are zero. CIS is equal to HF for the ground-state energy, although higher roots from the secular equations may be used as approximations to excited states. It has already been mentioned that only doubly excited determinants have matrix elements with the HF wave function different from zero, thus the lowest CI level which gives an improvement over the HF result is that which includes only doubly excited states, yielding the CID. Although the singly excited determinants have zero matrix elements with the HF reference, they enter the wave function indirectly as they have non-zero matrix elements with the doubly excited determinants. So that the only CI method is generally applicable for a large variety of systems is CISD. For molecular properties, the singly excited states thus allow the CI wave function to "relax" the MOs, i.e. letting the wave function respond to the perturbation.

Size Consistency, Performance, and Accuracy

Size consistency is the property that is required for any theoretical model incorporating electron correlation to be applicable to problems of chemical reactivity. It means that the method when applied to an ensemble of isolated molecules should give results which are additive for the energy and other properties. Unfortunately, any incomplete CI does not satisfy this requirement and its applications therefore must be treated with caution if comparison is made for properties of molecule of different size. The origin of this deficiency is well understood and the terms contained in the CI energy, which do not scale linearly with the number of particles, have been identified. The most convenient tool for the examination of size inconsistency in CI is the many-body perturbation theory. It was found that, unlike in the fourth- and higher-order many-body perturbation theory, the unphysical terms in CISD are not canceled and their cancellation is only achieved if quadruply and higher excited CSFs are included in the CI expansion. Complete cancellation is secured only by full CI, though it is believed that CISDTQ properties should be very near the full CI limit for chemical systems which can be well represented by a single restricted HF wave function. For dimer $(H_2O)_2$ and the double zeta basis set the CISDTQ size-inconsistency error amounts to 0.0003 au. This is considerably less than the CISD error of 0.0047 au. In general, we must expect that CISD does not provide results with the accuracy sufficient, for example, for thermo chemistry. This stimulated attempts to eliminate unphysical terms in the CISD energy in some computationally simple, though approximate way. Several formulas were suggested for the a posteriori correction of the CISD energy. The most popular among these is the Davidson correction:

$$\Delta E = (1 - c_0^2)(E_{CID} - E_{SCF}) \qquad (65)$$

where E_{CID} is the CID energy and C_0 is the expansion coefficient for the ground state CSF. Originally the Davidson correction was developed for CID but it is commonly used for correction of CISD energies.

It has been stated that CISDTQ properties are very near to the full CI data for systems which can be well represented by a single restricted HF wave function. Unfortunately, in spite of the progress made recently in CISDTQ calculation, the method cannot be advocated for general use because of the immense number of triply and quadruply excited CSFs. The method scales as n^{10}, where n is the number of active molecular orbitals, and it can be used only for the smallest molecular systems. On the other hand, the CISD method scales only as N^6, N being the number of (atomic) basis set functions, which makes the method amenable to routine calculations. In general, the errors in CISD energy predictions (heats of reactions, activation barriers) have to be expected to be considerably larger than that corresponding to the ‘chemical accuracy’ (1 kcal/mol^{-1}), even if the Davidson correction is applied. CISD fails particularly in those cases where the size-inconsistency effect is important.

If a higher accuracy is required, it is recommended to pass to the coupled cluster (CCs) theory, Basically, CCSD is also an N^6 procedure, but the test calculations showed that the timing ratio CCSD/CISD ranged from 4 to 8, though as with any comparison of two different methods, the ratio depends strongly on the efficiency of the two programs.

2.2 Symmetry Adapted Cluster and Symmetry Adapted Cluster Configuration (SAC/SAC-CI) Method

SAC theory for the ground state

SAC is abbreviation for the symmetry adapted cluster, the meaning of which will become clear later. It belongs to the cluster expansion approach, which was originated in the statistical theory of interacting atoms, in the theory of electron correlations in atoms and molecules.

Electron correlation is defined on the basis of the HF theory as

$$E_{corr} = E_{exact} - E_{HF} \qquad (66)$$

$$\chi_{\mathrm{corr}} = \Psi_{\mathrm{exact}} - \Psi_{\mathrm{HF}} \qquad (67)$$

where ‘exact’ stands for the exact solution of the non-relativistic Schrodinger equation. Since the HF model is independent particle model, electron correlations represent mainly the collisions of electrons scattering into unoccupied orbitals. We introduce an excitation operator T_I^+ which represents such a collision. For example, a collision of two electrons belonging to the occupied orbital φ_{i}, resulting in the scattering into the unoccupied orbital φ_{a}, is represented by the excitation operator T_{ii}^{aa},

$$T_{ii}^{aa} = a_{a\alpha}^{+}\, a_{a\beta}^{+}\, a_{i\alpha}\, a_{i\beta} \qquad (68)$$

$$T_{ii}^{aa}\,|0\rangle = \|\varphi_1\alpha\varphi_1\beta \ldots \varphi_a\alpha\varphi_a\beta \ldots \varphi_n\alpha\varphi_n\beta\|, \text{ where } |0\rangle = \Psi_g^{HF} \qquad (69)$$

Configuration interaction (CI) method is one of the most popular methods for including electron correlations. This method is based on the expansion theorem, and the correlated wave function is expressed as

$$\Psi^{CI} = B_0 \left|0\right\rangle + \sum_I B_I T_I^+ \left|0\right\rangle \tag{70}$$

where B_I are expansion coefficients. This method is simple and exact, but is usually slowly converging, especially for excited states. The dimension of the configurations easily reaches to the order of 10^8, though many efficient algorithms for handling such large matrices are proposed. Further, it is difficult to extract a physical meaning from such a large number of configurations. It is also difficult to solve many lower solutions of such a large matrix, which is necessary for studying shake-up spectra, for example.

The main factor of electron correlation is collisions of two electrons. In many electron systems, however, there is a chance for three, four and more electrons to collide each other. However, the probabilities for four collisions actually important are the products of pair collisions occurring at different places of the molecule. This is because the fluctuation potential for the electron correlation is very short range. When we introduce a sum of the excitation operation as

$$T = \sum_I C_I T_I^+ \tag{71}$$

The wave function including higher-order collisional effects is written as

$$\Psi_g = (1 + T + 1/2\, T^2 + 1/6\, T^3 + \ldots..) \left|0\right\rangle \tag{72}$$

where the terms T^2, T^3, etc., represent two pair collisions, three pair collisions, etc., and the factors 1/2, 1/6, etc., are due to the indistinguishability of pair collisions. Eq. (72) is more compactly written as

$$\Psi_g = \exp(T) \left|0\right\rangle \tag{73}$$

which is the cluster expansion. The suffix g again stands for the ground state. The theory based on this expansion in called coupled cluster (CC) theory. Hereafter, we call the term, $(1+T)\,|0\rangle$ as linked term and term, $(1/2\,T^2 + 1/6\,T^3 + \ldots..)\,|0\rangle$ as unliked term.

In the above formulation, we have introduced the operators T_I^+ representing two electron excitations (pair collisions). However, generally speaking, this is just an example, and we may take any operators physically important. An important example is to choose *T* as a sum of all single excitation operators,

$$\mathrm{T}^{(1)} = \sum_{i}^{occ} \sum_{a}^{unocc} C_i^a\, a_a^+\, a_i \qquad (74)$$

where *i* and a stand for the general spin orbital. Then we get Thouless theorem,

$$\Psi^{\mathrm{SD}} = N \exp(T^{(1)})\, \Phi^{\mathrm{SD}} \qquad (75)$$

where Φ^{SD} and Ψ^{SD} are different single determinants, *N* a normalization constant. This theorem states that the transformation of single determinants to another one is expressed by the operator *N* exp ($T^{(1)}$): the cluster expansion includes the *self-consistency of orbitals.*

We note that for open-shell systems, the single determinant Ψ^{SD} on the left hand side of eq. (75) is not a restricted determinant, but an unrestricted one which is not an eigenfunction of the spin-squared operator S^2. Generally, the wave function of the CC theory is not an eigenfunction of S^2, as actually reported for the CCSD wave functions for doublet radicals. In the linear expansions like CI, the solution of the secular equation is always symmetry-adapted, irrespective of the choice of the excited configurations, because the Hamiltonian is totally symmetric. However, this is not the case for the non-linear expansions like cluster expansion. Further, as explained below, coupled cluster expansion may involve a larger number of variables than that necessary for describing the state.

These difficulties do not occur when excitation operations are chosen to be symmetry adapted. Excitation operator S_I^+ are defined to be symmetry adapted when the configuration $S_I^+ |0\rangle$ is symmetry adapted. For totally symmetric singlet states, the symmetry adapted cluster (SAC) expansion are defined as

$$\Psi_g^{SAC} = \exp(S)\ |0\rangle \tag{76}$$

where

$$\mathrm{S} = \sum_I C_I S_I^+ \tag{77}$$

Since S_I^+ is totally symmetric, the unliked terms of eq. (76) are also totally symmetric. For open-shell states like doublet and triplet states, we need a symmetry projector Q as

$$\Psi_g^{SAC} = Q \exp(S)\ |0\rangle = [1 + S + Q\,(1/2S^2 + 1/6S^3 + \ldots)\ ]\ |0\rangle \tag{23}$$

where $|0\rangle$ is a restricted determinant and Q applies only to the unliked terms, since the linked term is already symmetry adapted. The SAC expansion defined by eq. (76) is thus different from the CC expansion given by eq. (73). Table 1 is summarized the differences in schematic way.

Appendix Table A1 Schematic summary of the differences of the SAC expansion from the conventional cluster expansions[a].

Expansion	Linked term	Unliked term[b]	Number of independent variables[c]	Symmetry[d]
exp(T) $\|0\rangle$	$T\|0\rangle$	$T_I\, T_J\,\|0\rangle$	Larger	Mixed
Qexp(T) $\|0\rangle$	$QT\|0\rangle \rightarrow S\|0\rangle$	$Q\,T_I\, T_J\,\|0\rangle$	Larger	Pure
Qexp(S) $\|0\rangle$	$S\|0\rangle$	$Q\,S_I\, S_J\,\|0\rangle$	Just as required	Pure

[a] The operators T_I are not symmetry-adapted, but the operators S_I are symmetry-adapted. [b] Only the second-order unliked terms are given. [c] The number of the independent variables included in each expansion is compared with that necessary for the description of the system under consideration. [d] Symmetry of the total wave function.

Now the solution of SAC theory was considered. In the SAC expansion, the unknown variables C_I are associated to the linked excitation operator S_I^{+}, so that we require the Schrodinger equation, $H\text{-}E_g \left|\Psi_g^{SAC}\right\rangle = 0$, within the space of the linked configurations as

$$\langle 0|\; H\text{-}E_g \left|\psi_g^{SAC}\right\rangle = 0 \tag{78a}$$

$$\langle 0|\; S_I(H\text{-}E_g) \left|\Psi_g^{SAC}\right\rangle = 0 \tag{78b}$$

We have the same number of equations as the number of the unknown variables, This solution is called non-variational solution.

The variational solution is obtained by applying the variational principle to the SAC wave function and we obtain,

$$\left\langle \Psi_g^{SAC}\right|\; S_I(H\text{-}E_g) \left|\Psi_g^{SAC}\right\rangle = 0 \tag{79a}$$

$$\left\langle \Psi_g^{SAC} \right| (H\text{-}E_g)\, S_I \left| \Psi_g^{SAC} \right\rangle = 0 \qquad \text{(79b)}$$

This equation is valid *only* for the SAC expansion, but not for the CC expansion, because of the reason summarized in Table 1. Generally, the variation solution is more difficult than the non-vairational one, because former involves the intergrals between the umliked terms. However, we believe, as long as the wave function itself is accurate, the difference between the variational and non-variational solutions should be small.

It is shown that eq. (79b) is the *generalized Brillouin theorem*. In comparison with eq. (80).

$$\left\langle \Psi_g^{HF} \left| \mathrm{H} \right| \phi_i^a \right\rangle = 0 \qquad \text{(80)}$$

where Ψ_g^{SAC} corresponds to Ψ_g^{HF} and $S_I^{+}\left| \Psi_g^{SAC} \right\rangle$ does to ϕ_i^a. As the Brillouin theorem is a key equation in the HF/SECI theory, the generalized Brillouin theorem given by eq. (79b) is a key equation in the theoretical framework of the SAC/SAC-CI theory. The SAC theory has the following properties. The first three are common to the CC theory.

(1) It effectively involves higher-order effects of electron collisions. It describes dynamic correlations quite effectively.
(2) It is size consistent or size extensive, so that it correctly describes the energy change in the dissociation process such as $X_n \rightarrow nX$. This property is a direct consequence of the exponential, since

$$\exp(A)\exp(B) = \exp(A+B) \qquad \text{(81)}$$

when the operators A and B are commutable.

(3) It includes self-consistency. This property is best represented by the Thouless' theorem given by eq. (75). It guarantees that the cluster expansion is *independent* of a choice of the reference orbitals, when we include all the single excitation operations.

(4) The SAC theory defines not only the SAC wave function itself Ψ_g^{SAC} for the ground state, but also the excited functions which span the basis for excited states. The SAC-CI theory is based on this property. This property is probably the most important property, among others, and is valid only for the SAC theory.

SAC-CI theory for excited, ionized, and electron attached states

It was thought for a long time that the description of electron correlations in excited states is much more difficult than that in the ground state. Excited states are generally open shells and are not represented by a single Slater determinant. Many different states of many different symmetries and natures are involves in a narrow energy range, which makes it difficult to suppose a single general theory in a useful form. However, this is not the case in the SAC-CI theory. By using the SAC-CI method, we can *easily* calculate the correlated wave function of the excited, ionized and electron attached states, as explained in the following.

The electron correlations in the excited state will be described on the basis of those in the ground state. Approximately, excitations and ionizations involve only one or two electrons, and most other electrons lie essentially in the same orbitals as in the ground state. Therefore, the electron correlations in the excited state should be able to be compactly described by considering only some modifications to the ground-state electron correlations.

The excited functions $\{\Phi_K\}$ by using the SAC wave function was written as

$$\Phi_K = P S_K^+ \Psi_g^{SAC} \qquad (82)$$

where P is the operator which projects out the ground state wave function,

$$P = 1 - \left|\Psi_g^{SAC}\right\rangle \left\langle\Psi_g^{SAC}\right| \qquad (83)$$

and $\{S_K^+\}$a set of the excitation operations involving the excitations under consideration in a orbital picture. From the generalized Brillouin theorem of the SAC theory, eq. (79b), it is easily shown that the functions $\{\Phi_K\}$ satisfy

$$\left\langle\Phi_K \middle| \Psi_g^{SAC}\right\rangle = 0, \qquad \left\langle\Phi_K \middle| H \middle| \Psi_g^{SAC}\right\rangle = 0 \qquad (84)$$

These equation shows, that *the set of the functions spans the space for the excited states.* We therefore describe the excited state by *a linear combination* of the functions $\{\Phi_K\}$,

$$\Psi_e^{SAC-CI} = \sum_K d_K \Phi_K \qquad (85)$$

which is the SAC-CI theory.

Obviously, the SAC-CI wave function for the excited state satisfied the correct relations with the SAC ground state,

$$\left\langle\Psi_g^{SAC} \middle| \Psi_g^{SAC-CI}\right\rangle = 0, \quad \left\langle\Psi_g^{SAC} \middle| H \middle| \Psi_g^{SAC-CI}\right\rangle = 0 \qquad (86)$$

Applying the variational principle to eq. (86) for solving the unknown variables $\{d_K\}$, we obtain

$$\left\langle\Phi_K \middle| H - E_e \middle| \Psi_g^{SAC-CI}\right\rangle = 0 \qquad (87)$$

Different solutions of eq. (86), which correspond to different excited states, satisfy

$$\left\langle \Psi_e^{SAC-CI} \middle| \Psi_f^{SAC-CI} \right\rangle = 0, \qquad \left\langle \Psi_e^{SAC-CI} \middle| H \middle| \Psi_f^{SAC-CI} \right\rangle \tag{88}$$

Since, they are the solutions of the common secular equation. Thus, the SAC-CI wave function satisfies the correct relations with the ground state and with the other excited states. This is very important when we consider the properties, like transitions and relaxations, which interconnect different states.

In the above formulation, we have considered implicitly the excited states having the same symmetry as the ground state. However, the SAC-CI theory is also valid for the excited states having different symmetries (e.g., triplet), and for the ionized and electron attached states. We generalize eq. (82) as

$$\Phi_{\mathrm{K}} = P R_K^+ \Psi_g^{SAC} \tag{89}$$

where $\{R_K^+\}$ represents a set of excitation, ionization, and/or electron attachment operators. In any cases, eqs. (83)-(88) are valid.

Though, the above formulation of the SAC-CI theory is variational and non-variational formulation. The non-variational SAC-CI solution is obtained by projecting the Schrodinger equation onto the space of the linked configurations,

$$\left\langle 0 \middle| R_K (H - E_e) \middle| \Psi_g^{SAC-CI} \right\rangle = 0 \tag{90}$$

Referring to eq. (79), we note that in the non-variational case, the SAC and SAC-CI wave functions satisfy the common set of equations. In particular, when we consider the excited states belonging to the same symmetry as the ground state, the operator $\{R_K^+\}$ in eq. (88) are actually $\{S_I^+\}$. The solutions of the Schrodinger equation belonging to different eigenvalues are orthogonal and Hamiltonian orthogonal. Therefore, we obtain eqs. (86) and (88) within the space of the liked operators under consideration. These equations are quite important for the theoretical consistency of the different states under consideration.

Practically, the non-variational solution is easier than the variational one by the reason similar to that stated for the SAC solution, but we have to diagonalize non-symmetric matrices. When the SAC-CI program was first coded, it was no efficient method for diagonalizing non-symmetric matrices of large dimentions, Therefore, we had to prepare the algorithm of iterative diagonaliztions of non-symmetric, extending the Davidson ‘s algorithm for symmetric matrices.

As the SAC theory is exact, the SAC-CI theory is also exact. Though the introduction of the SAC-CI theory so far given is rather formal and straightforward, it has some interesting physics. First, omitting the projector, or including the identity operator into $\{ R_K^+ \}$, then the SAC-CI wave function was written as

$$\Psi_e^{SAC-CI} = \Re \ \Psi_g^{SAC} \tag{91a}$$

where the excitatory $\Re$ (a king of reaction operator) is defined as

$$\Re = \sum_K d_K R_K^+ \tag{91b}$$

We already know that the SAC wave function well describes the electron correlation of the ground state. The excitatory $\Re$ describes the excitation starting from the electron correlation involved in the SAC ground state Ψ_g^{SAC}.

Generally, excitation is only one or two electron processes and most other electrons lie in the situation (orbitals) similar to those in the ground state. Therefore, it is clever to start from the ground-state electron correlation and describe only the modifications caused by the excitation. eqs. (91a) and (91b) just represent such as an idea, which is the ***transferability*** of electron correlations between ground and excited states. This method is much easier than calculation all of the electron correlations of each state from the beginning. Since the ground-state electron correlation is easier to calculate than the excited state one, when we calculate from the beginning, we first calculate it by the SAC method and then utilize it in the SAC-CI method for calculating the excited-state correlations based on its transferability. For this reason, the SAC-CI expansion is much easier and more rapidly convergent than ordinary CI.

The SAC-CI wave function is also written in the form

$$\Psi_e^{SAC-CI} = \exp\left(\sum_I C_I S_I^+\right)\sum_K d_K R_K^+ |0\rangle \qquad (92)$$

which has the structure of multi-reference CI. The configurations $R_K^+|0\rangle$ represent the reference configurations and the operator exp $(\sum_I C_I S_I^+)$ represents the excitations from these reference configurations. In the latter, we use the coefficients $\{C_I\}$ determined for the ground state, which is based on the transferability of electron correlations between the ground and excited states. The dimension of the SAC-CI method is the number of the reference configurations which are typically in the order of 10^3-10^5, not like limited to ~10. Therefore, in the SAC-CI method, there is almost no ambiguity in the choice of the 'main reference' configurations in contrast to the ordinary multireference CI method.

The SAC-CI method can be applied to various kinds of excited states by using appropriate excitation operators. It can be applied to excited states, ionized states, and electron attached states having spin multiplicities of singlet, doublet, triplet and up to septet. An important merit is that we can calculate these different electronics states in a *same accuracy*. We *can directly compare* the energies and the wave functions of different electronic states: a property quite important and useful in actual applications. *Thus using the SAC-CI method, we can study chemistry and physics involving the ground state and excited states of various spin multiplicities.*

2.3 Time Dependent Density Functional Theory

A DFT method that is strongly analogous to RPA is called time-dependent DFT (TDDFT). In this case, the Kohn-Sham (KS) orbital energies and various exchange integrals are used in place of matrix elements of the Hamiltonian. TDDFT is usually most successful for low-energy excitations, because the KS orbital energies for orbitals that are high up in the virtual manifold are typically quite poor. Casida, and coworker (1998) have suggested that TDDFT results are most reliable if the following two criteria are met: (i) the excitation energy should be significantly smaller than the molecular ionization potential (note that excitations from occupied orbitals below the HOMO are allowed, so this is not a tautological condition) and (ii) promotion(s) should not take place into orbitals having positive KS eigenvalues.

Time-dependent density functional theory is widely used as a reliable method for the prediction of electronic excitation processes and other fast time-dependent phenomena involving the electronic response to an external perturbation. Density functional theory (DFT) accounts for the electron correlation of a system in the ground state by virtue of approximations to the exact but unknown exchange-correlation functional. Thus, TDDFT can also, in principle, incorporate a large fraction of the effects of electron correlation in an excited state within the framework of single-excitation theory. In practice, the accuracy of TDDFT employing the most widely available exchange-correlation functionals, which are approximations to the true functional and so-called adiabatic approximation, has been varied. For vertical excitation energies to low-lying valence excited states, TDDFT with these approximate functionals has proven quite accurate, significantly outperforming the Hartree-Fock based analogues, such as CIS and TDHF. However, for high lying excited states or Rydberg excite states, TDDFT underestimates the excitation energies by up to 1 eV or more.

Ground-state DFT is based on the papers by Hohenberg and Kohn, and by Kohn and Sham. The main results are that the density of system is identical to the density of an associated noninteracting particle system moving in local potential v_s (r) defined by the Khon-Sham equations (atomic units are used throughout):

$$\left[-\frac{1}{2}\nabla^2 + v_s[\rho(r)]\right]\varphi_i(r) = \varepsilon_i\varphi_i(r) \tag{93}$$

Here the local potential $v_s[\rho](r)$ is the so-call Kohn-Sham potential, consisting of the external potential v_{ext} (the Coulomb field of the nuclei and external field if present), the Hatree potential v_H , which is trivially calculated from the density, and the *xc* potential v_{xc} which is the only unknown part:

$$v_s(r) = v_{ext}(r) + v_H(r) + v_{xc}(r) \tag{94}$$

The Kohn-Sham orbitals ϕ_i move in the effective field v_s which depends upon the electron density ρ(r). This density is exactly obtained by summing the squares of the Kohn-Sham orbitals and multiplying by their occupation numbers n_i.

$$\rho(r) = \sum_{i}^{occ} n_i |\varphi_i(r)|^2 \tag{95}$$

As the KS potential $v_s(r)$ and the density ρ(r) are inter-dependent, the equation have to be solved in a Self-Consistent Field (SCF) procedure, which means that one iteratively adapts the effective potential v_s and the density ρ until the difference in the energy between two subsequent cycles is sufficiently small. In the most straightforward fashion, this can be performed by mixing the density of the previous cycle with a small part of the density in the present cycle. This “simple damping” approach usually converges very slowly, and in practice the Direct Inversion in the Iterative Subspace (DIIS) procedure by Pulay and co-workers, is much to be preferred. In the DIIS approach, not only the results of previous cycle, but the results of all, or many, previous cycles are taken into account, in order to obtain the optimal guess for the next cycle. If one is close to self-consistency, this procedure converge the SCF equation above.

In order to solve the KS equations an approximation for the exchange-correlation (*xc*) potential $v_{xc}(r)$ is required and the simplest one is the LDA which is based upon the local density of the system. The GGAs go beyond this and take the local gradient of the density into account as well, allowing for a much improved accuracy in the results for energies and geometries. Many other approximations, for examples those based directly on the KS orbitals, are also available.

The usual ground state DFT sheme enables one to determine the density, and consequently the dipole moment, of a molecule with or without external electric fields. This affords the determination of the static polarizability and hyperpolarizability tensors α, β and γ by performing calculations in small electric fields of varying magnitudes and directions. In this so-call finite field (FF) approach, the tensor are then determined from finite difference techniques. The main advantage of this approach is that no programming work is needed. Any standard DFT code will allow the determination of static properties in this manner. However, for the determination of higher order tensors, such as γ, one need very well converged solution to the KS equations in order to make reliable predictions, which may be technically hard to achieve and which will certainly lead to considerable increase in CPU time consuming.

The most fundamental disadvantage of the FF approach, however, is that one has access to static properties only. The frequency-dependent polarizability and hyperpolarizabilty tensors are not accessible. Excitation energies and oscillator strengths can also not be obtained from the FF calculations. This is and important drawback of the FF approach, as it makes a direct comparison with experimental results are impossible. Especially for hyperpolarizabilities, it is known that there are substantial differences between the frequency-dependent and zero frequency results.

If one is interested in the time dependent properties mentioned above, a time dependent theory is required. In the DFT framework, this means that one has to start from the time dependent KS (TDKS) equations as derived by Runge and Gross;

$$i\frac{\partial}{\partial t}\varphi_i(r,t) = \left[-\frac{\nabla^2}{2} + v_s(r,t)\right]\varphi_i(r,t) \equiv F_s\varphi_i(r,t) \qquad (96)$$

The time dependent KS potential $v_s(r,t)$ is subdivided in the same manner as its static counterpart:

$$v_s(r,t) = v_{ext}(r,t) + v_H(r,t) + v_{xc}(r,t) \qquad (97)$$

the Hatree potential being explicitly given by:

$$v_H(r,t) = \int dr' \frac{\rho(r',r)}{|r-r'|} \qquad (98)$$

and the time dependent *xc* potential $v_{xc}[\rho](r,t)$ being an unknown functional of the time dependent density $\rho(r,t)$ now given by:

$$\rho(r,t) = \sum_i^{occ} n_i |\varphi_i(r,t)|^2 \qquad (99)$$

If a certain approximation for the time dependent *xc* potential v_{xc} (r,t) has been chosen, the TDKS equations can be solved iteratively to yield the time dependent density of system, which may be exposed to an external time dependent electric field. If one is interested in the effects due to extremely large laser fields, the perturbative expansion of the dipole moment become meaningless, and the TDKS equations have to be solved non-peturbatively. This has until now been performed for atoms, by Hirata and coworker (1999), and more recently also by others, and gives access to such effects as higher harmonic generation (HHG), which are not accessible in a perturbative approach. The drawback of this is that the calculations are very time consuming, forbidding the treatment of medium-sized molecules. If one restricts oneself to properties which are accessible through perturbative methods, as we will do here, a much more efficient approach is possible, allowing the treatment of large molecules (>100 atoms).

2.4 An Intermediate Neglect of Differential Overlap (INDO) Technique for Spectroscopy

The intermediate neglect of different overlap (INDO) is based on the simplest molecular orbital theory that properly accounts for the two-electron terms required in spectroscopy. INDO/s, where the one-center core integrals are obtained from ionized potentials only, rather than from ionization potentials and electron affinities, is used to calculate the ground-state configuration in terms of molecular orbital coefficients and eigenvalues.

In the molecular orbital model, using the unrestricted Hartree-Fock theory, we are interested in solving the Hartree-Fock equations

$$F^{\alpha}C^{\alpha} = C^{\alpha}E^{\alpha} \qquad (100)$$

for an orthogonalized atomic basis set $\{\phi_{\mu}\}$, where E^{α} is the diagonal matrix of eigenvalues for the α spin molecular orbital, C^{α} is a square matrix the *i* th column of which is the molecular orbital coefficients of the *i* th molecular orbital ϕ_i^{α}

$$\phi_i^{\alpha} = \Sigma c^{\alpha}_{i\mu}\,\phi_{\mu} \qquad (101)$$

F^{α} is the Fock or energy matrix

$$F^{\alpha} = H + J - K^{\alpha} \cong H + G^{\alpha} \qquad (102)$$

and similar expressions are appropriate for β spin matrices and orbitals. In the above, H is the one-electron matrix, and $G^{\alpha} = J - K^{\alpha}$ is the two-electron matrix consisting of Coulomb terms minus exchange. The one-electron matrix H is specified by

$$H^{AA}_{\mu\mu} = U^{AA}_{\mu\mu} - \sum_{B \neq A} Z_B(\phi_\mu \left| R_B^{-1} \right| \phi_\mu) \qquad (103)$$

$$U^{AA}_{\mu\mu} \cong (\phi_\mu \left| -\nabla^2/2 - Z_A/R_A \right| \phi_\mu) \qquad (104)$$

$$H_{\mu\nu} = (\phi_\mu \left| -\nabla^2/2 - \sum_A Z_A/R_A \right| \phi_\mu) \qquad (105)$$

Using the INDO model of Pople, Santry, and Segal we obtained

$$H^{AA}_{\mu\mu} = U^{AA}_{\mu\mu} - \sum_{B \neq A} Z_B \gamma_{AB} \qquad (106)$$

$$H^{AA}_{\mu\nu} = 0 \qquad (107)$$

$$H^{AB}_{\mu\nu} = (\beta^0_{A,\mu} + \beta^0_{A,\mu})\,\overline{\Delta}_{\mu\nu}/2 \qquad (108)$$

$$\gamma_{AB} = \left\langle \overline{\phi}_\mu \overline{\phi}_\mu \middle| \overline{\phi}_\nu \overline{\phi}_\nu \right\rangle \cong \int d\tau(1)d\tau(2)\overline{\phi}_\mu(1)\overline{\phi}_\mu(1)r_{12}^{-1}\overline{\phi}_\upsilon(2)\overline{\phi}_\upsilon(2) \qquad (109)$$

$\{\beta^0_{A,\mu}\}$ are atomic parameters, chosen empirically to give best agreement with experiment. The same parameter is used for either an s or p atomic orbital, $\beta^0_{A,s} = \beta^0_{A,p}$, but a different parameter is chosen for the d orbitals. $\overline{\Delta}_{\mu\nu}$ is a proportionality constant, usually the orbital overlap calculated treating ϕ_μ and ϕ_ν as Slater-type orbitals, or an integral simply related to the overlap. γ_{AB} is the two-electron Coulomb integral calculated treating ϕ_μ of atom A and ϕ_ν of atom B as if both were of s symmetry. Such an approximation is required by rotational invariance. Since the orbital exponents of s and p atomic orbitals are chosen the same for a given atom,

$\gamma^{AB}{}_{ss} = \gamma^{AB}{}_{sp} = \gamma^{AB}{}_{pp} = \gamma_{AB}$. However, the exponent of a d atomic orbital is not the same as an s and p.

In the unrestricted Hartree-Fock formalism that is used here, the G matrix elements are given by

$$G^{\alpha}{}_{\mu\nu} = \sum_{\sigma\lambda} P_{\sigma\lambda} \langle \mu\nu | \sigma\lambda \rangle - P^{\alpha}{}_{\sigma\lambda} \langle \mu\sigma | \nu\lambda \rangle \tag{110}$$

with a similar expression for the β electron G^{β} matrix. Here P^{α} is the first-order α spin density matrix or, in the orthogonalized set envisioned here, the α spin charge and bond order matrix

$$P^{\alpha}{}_{\mu\nu} = \sum_{a}^{MO} C^{\alpha}{}_{\mu a} C^{\alpha}{}_{\nu a} n_a \tag{111}$$

Where $n_a = 0$ or 1, the occupancy of $\phi^{\alpha}{}_{a}$, and P is the total first-order density

$$P = P^{\alpha} + P^{\beta} \tag{112}$$

Under this formalism, for a closed-shell system

$$P^{\alpha} = P^{\beta} = 1/2P \tag{113}$$

Invoking the INDO model simplifies eq. (109) greatly:

$$G^{\alpha}{}_{\mu\mu} = \sum_{\sigma\lambda}^{A} [P_{\sigma\pi} \langle \mu\mu | \sigma\lambda \rangle - P^{\alpha}{}_{\sigma\lambda} \langle \mu\sigma | \nu\lambda \rangle] + \sum_{\sigma \notin A} P_{\sigma\sigma} \gamma_{\sigma\mu} \ ; \ \mu \in A \tag{114}$$

$$G^{\alpha}{}_{\mu\nu} = \sum_{\sigma\lambda}^{A} [P_{\sigma\pi} \langle \mu\nu | \sigma\lambda \rangle - 1/2 P^{\alpha}{}_{\sigma\lambda} \langle \mu\sigma | \nu\lambda \rangle] \ ; \ \mu, \nu \in A \tag{115}$$

$$G^{\alpha}_{\mu\nu} = - P^{\alpha}_{\mu\nu}\, \gamma_{\overline{\mu\nu}} \;;\; \mu \in A, \nu \in B, A \neq B \tag{116}$$

with similar expressions for G^{β}.

The two-electron two-center Coulomb integrals $\gamma_{\overline{\mu\nu}}$ are required for eq. (109) and for eq (116). For spectroscopy, however, a great deal of experience has been gained by using Coulomb integrals chosen semi-empirically.

The two-electron Coulomb integrals are evaluated from a modified Mataga-Nishimoto formula

$$\gamma_{AB} = \frac{f_{\gamma}}{2f_{\gamma}/(\gamma_{AA} + \gamma_{BB}) + R_{AB}} \tag{117}$$

where R_{AB} is the distance between the two centers in Bohr radii, γ_{AA} is obtained from

$$\gamma_{AA} = F^{0}(AA) = I_A - A_A \tag{118}$$

as the difference between the ionization potential and electron affinity of an s, p or d electron. The formula is modified by the introduction of the parameter f_{γ} as suggested by Weiss, which set equal to 1.2. This value has been extensively used and has proven very successful in the calculation of spectra of conjugated systems. Since values of $I_A - A_A$ are similar for s and p orbitals, we make the approximation that $\gamma_{\overline{AA}} = \gamma_{\overline{ss}} = \gamma_{\overline{sp}} = \gamma_{\overline{pp}} = F^{0}(AA)$ as before.

The INDO spectroscopic model has been parameterized by comparison of experimental spectra with calculated results obtained after extensive studies with singly excited configurations in a configuration interaction treatment. This basic model has been extended to include members of the first transition series (Zerner *et al.*, 1979), and has been applied to rather large systems in which the role of higher excited configurations (double excited, triple excited, etc., as opposed to higher *energy* configurations) is uncertain. Although use of semi-empirical two-electron integrals (γ) and empirical resonance integrals (β) might be expected to include the effect of higher energy excitations in an average way, no such parameterizations can be expected to compensate for multiple excited configurations if those configurations are actually in the spectroscopic region of interest, or if a given double excitation heavily mixes with the reference configuration in the mathematical description of the ground state. In these cases, certain higher excitations *must* be included explicitly. Preliminary investigations seem to indicate that higher excitation excitations can be included in the model without extensive re-parameterizations. Nevertheless, some systems cannot be well described without these higher excitations, even with the given semi-empirical parameterizations. The frequency of these more difficult to handle systems is expected to increase with increasing molecular size, and the effect will be aggravated by the presence of a transition metal. The presence of two like transition metals in most complexes will require consideration of higher excitations in the description of both ground and excited states.

In addition to the model being grounded on singly excited configuration interaction, which is not a severe limitation in most cases, the model is founded on basis set of valence-type orbital. Since Rydberg-type orbitals are not included in the atom basis, Rydberg-type states cannot be described. This is as severe a limitation on small molecules where the Rydberg states are among the lowest lying excited states as exclusion of higher excitations is for very large systems, where they are low lying. For most molecules Rydberg states might be expected to make their appearance 2-3 eV below the first ionization potential. In this region of the spectrum the density of states is quite high. The appearance of broad absorptions usually found within 2-3 eV of the first ionization potential for large systems may have as much to do with the presence of many electronic origins as it have to do with the vibration broadening usually considered.