Computational quantum chemistry methodology and applications

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Abstract

Quantum chemistry is based on the postulates of Quantum Mechanics, where a many-electron system is described by a wavefunction which can be found by solving the Schrödinger equation. In practice the Schrödinger equation cannot be solved exactly and approximations have to be made. Its solution by the use of HFR self consistent field theory and its implementations for computation such as ab initio and semi-empirical methods are reviewed. Finally, some molecular quantities and properties that can be calculated will be presented.

Keywords: Quantum chemistry, Schrödinger equation, HFR self consistent field, ab initio, semi-empiric

Introduction

Computational quantum chemistry have become an essential tool in the study of atoms and molecules and, increasingly, in modeling complex systems such as those arising in biology and materials science. The underlying core technology is computational solution of the electronic Schrödinger equation; giving the positions of collection of atomic nuclei, and the total number of electrons in the system, will result in the electronic energy, electron density, and other molecular properties by means of a well defined approximation.

There are two groups of computational quantum chemistry: (i) ab initio methods, and (ii) semi-empirical techniques. Ab initio is a group of methods in which molecular structures can be calculated using nothing but the Schrödinger equation, the values of the fundamental constants and the atomic numbers of the atoms present, while the semi-empirical techniques use empirical data to provide the input into the mathematical models.

Methodology

Within the Born-Oppenheimer approximation, the Schrödinger equation for a many-electrons system is

\[ \hat{H}_{el} \Psi = E_{el} \Psi \]  

(1)

The electronic wavefunction \( \Psi \) depends on the electronic coordinates, \( E_{el} \) is the electronic energy and the Hamiltonian is

\[ \hat{H}_{el} = \sum_{\mu} \hat{H}(\mu) \]  

(2a)

where

\[ \hat{H}(\mu) = \hat{H}^c(\mu) + \frac{1}{2} \sum_{\nu \neq \mu} \frac{1}{r_{\mu\nu}} \]  

(2b)

and

\[ \hat{H}^c(\mu) = - \frac{1}{2} \nabla^2 \mu - \sum_{A} \frac{Z_A}{r_{\mu A}} \]  

(2c)

\( Z_A \) is the atomic charge of the A-th core, \( r_{\mu A} \) is the distance between the \( \mu \)-th electron and the the A-th core, while \( r_{\mu \nu} \) is the distance between the \( \mu \)-th and the \( \nu \)-th electrons.

The electronic wavefunction \( \Psi \) is expressed as a Slater determinant of all spin-orbital occupied by the electrons. For closed shell

\[ \Psi(1,2,...,N) = \frac{1}{\sqrt{N!}} \left| \phi_1^\sigma(1) \phi_2^\sigma(2) \phi_3^\sigma(3) ... \phi_N^\sigma(N) \right|_T \]  

(3a)

where a spin-orbital \( \phi_\sigma^I \) means the product of spatial molecular orbital \( \phi \) and spin state \( \sigma (\alpha \text{ or } \beta) \) of the electron occupied the spatial molecular orbital \( \phi_i \);

\[ \phi_\sigma^I = \phi_i \sigma \]  

(3b)

The electron-electron potentials in eq. (2b) can not be evaluated exactly, since the electronic coordinates of the two electrons are involved simultaneously. Hartree and Fock have considered the potential experienced by the \( \mu \)-th electron as the average potential of the others. Then the one-electron Hamiltonian \( \hat{H}(\mu) \) expressed as

\[ \hat{\tilde{F}}(\mu) = \hat{H}^c(\mu) + \sum_n \frac{N^2}{2} \tilde{J}_n(\mu) - \tilde{K}_n(\mu) \]  

(4a)

where
\[ \hat{J}_n(\mu)\varphi_m(\mu) = \left[ \varphi_n^*(\nu) \frac{1}{r_{\nu\mu}} d\tau_\nu \right] \varphi_m(\mu) \] (4b)

\[ \hat{K}_n(\mu)\varphi_m(\mu) = \left[ \varphi_n(\nu) \varphi_m^*(\nu) \frac{1}{r_{\nu\mu}} d\tau_\nu \right] \varphi_n(\mu) \] (4c)

As an effective one-electron Hamiltonian, Hartree-Fock introduced the one-electron Schrödinger equation

\[ \hat{\mathcal{F}}(\mu)\varphi_n(\mu) = \varepsilon_n\varphi_n(\mu) \] (5)

where \( \varepsilon_n \) is the energy of the molecular orbital \( \varphi_n \).

According to the Roothaan’s MO LCAO approximation, a spatial molecular orbital can be denoted as a linear combination of atomic orbitals involved in the electronic system,

\[ \varphi_n = \sum_i c_{in} \chi_i \] (6a)

The atomic orbitals used eq. (6a) are called basis functions. For a normalized spatial molecular \( \varphi_n \), the coefficients \( \{c_{in}\} \) fulfill

\[ \sum_i c_{in} c_{jn} S_{ij} = 1 \] (6b)

where

\[ S_{ij} = \int \chi_i^* \chi_j d\tau \] (6c)

Using eq’s (5) and (6a-c) we can perform a secular equation

\[ \sum_i \left( F_{ij} - \varepsilon_n S_{ij} \right) c_{in} = 0 \] (7a)

where

\[ F_{ij} = \int \chi_i^* \hat{\mathcal{F}}(\mu) \chi_j d\tau \] (7b)

Using eq’s (4a-c) and (6a), the detail of eq. (7b) is

\[ F_{ij} = H_{ij} + \sum_{k,l} P_{ik} \left[ \langle j|k|l \rangle - \frac{1}{2} \langle i|k|j \rangle \right] \] (7c)

where

\[ H_{ij} = \int \chi_i^*(\mu) \hat{H}^i(\mu) \chi_j(\mu) d\tau_{\mu} \] (7d)

\[ \langle j|k|l \rangle = \int \chi_j^*(\mu) \chi_k(\mu) \chi_l(\nu) \frac{1}{r_{\nu\mu}} d\tau_{\mu} d\tau_{\nu} \] (7e)

\[ \langle i|k|j \rangle = \int \chi_i^*(\mu) \chi_k(\mu) \chi_j(\nu) \frac{1}{r_{\nu\mu}} d\tau_{\mu} d\tau_{\nu} \] (7f)

\[ P_{ik} = \sum_{\alpha\beta} 2\varepsilon_{\alpha\beta}^* c_{i\alpha} c_{k\beta} \] (7g)

Eq. (7g) is known as the charge density matrix. The matrix form of eq. (7a) is

\[
\begin{bmatrix}
F_{11} - \varepsilon_1 & F_{12} - \varepsilon_2 & \cdots & F_{1N} - \varepsilon_N \\
F_{21} - \varepsilon_1 & F_{22} - \varepsilon_2 & \cdots & F_{2N} - \varepsilon_N \\
\vdots & \vdots & \ddots & \vdots \\
F_{N1} - \varepsilon_1 & F_{N2} - \varepsilon_2 & \cdots & F_{NN} - \varepsilon_N \\
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_N \\
\end{bmatrix} = 0
\]

The orbital energies \( \{\varepsilon_n\} \) can be obtained from \( \text{det}(F_{ij} - \varepsilon_n S_{ij}) = 0 \). If all \( \{F_{ij}\} \) and \( \{S_{ij}\} \) are already known, one may then obtain the molecular orbital energies \( \{\varepsilon_n\} \) from the determinant, and substitution each value of \( \varepsilon_n \) into eq. (8) will result in the corresponding coefficients \( \{c_{in}\} \) for its spatial molecular orbital \( \varphi_n \).

Using above equations, one can design a computer program to solve eq. (7a). Before that, the matrix elements \( \{F_{ij}\} \) and \( \{S_{ij}\} \) have to be calculated. As shown in eq. (7c), a matrix element \( F_{ij} \) needs all of matrix elements \( \{P_{ik}\} \). However, each matrix element \( P_{ij} \) can only be determined by using coefficients \( \{c_{in}\} \) and \( \{c_{jm}\} \) which are the solution of eq. (7a) itself. Therefore, the computation must be performed iteratively; this way of computation is called as a self-consistent field (SCF) computation. The computation is not iteratively if the matrix elements \( \{F_{ij}\} \) are parameterized such as in Hückel method.

The molecular energy is a sum of electronic energy and the core-core repulsion energy,

\[ E = E_{el} + \sum_{A} \sum_{B(\neq A)} E_{AB} \] (9a)

where

\[ E_{el} = 2 \sum_{n} \frac{N/2}{n} \sum_{n} \sum_{m} \left( 2J_{nm} - K_{nm} \right) \] (9b)

In ab initio method, all of one- and two-electron integrals in eq.’s (7d-7f) are calculated using atomic orbitals \( \{\chi_i\} \) as basis functions. Each atomic orbital is expressed as a Slater-type orbital (STO) given by

\[ \chi_i = \frac{(2\xi/a_n)^{n+1/2}}{(\sqrt{2\pi})^n} r^{-n-1} e^{-\xi r/a_n} Y_{nm}(\theta, \phi) \] (10)

where \( \xi \) is the exponent of the orbital, while subscript \( i \) represents the quantum numbers \( n, l, m \), i.e. principle, orbital and magnetic orbital, respectively. For practical calculations those orbitals are approximated by a linear combination of Gaussian basis functions (GTO):
Subscript $u$ represents exponent $\alpha$ and numbers $i, j, k$. The exponent $\alpha$ and contraction coefficients $d_{uv}$ must be determined by fitting to an STO or by optimizing the energy in ab initio calculations on atoms. Once these values are determined they define a standard basis set, and are not changed in further calculations.

Several standard basis sets are nowadays commonly used. The most popular are the basis sets designed by Pople and his coworkers [1]. The so-called minimal basis sets have one orbital basis per two inner shell electrons and one basis orbital for each valence atomic orbital. Thus, for first-row elements there are basis functions resembling 1$s$, 2$s$, 2$p_x$, 2$p_y$, 2$p_z$ atomic orbitals. The STO’s are replaced by $n$ GTO’s (STO-nG). The common minimal basis set is the STO-3G basis. In order to increase the flexibility of the SCF wavefunction one can increase the number of basis functions per atom. In Double Zeta basis sets there are two functions for each atomic orbital of the minimal basis, one which is closer to the nucleus, the other allowing for electron density to move away from the nucleus. For the first row elements this gives 1$s$, 1$s’$, 2$s$, 2$s’$, 2$p_x$, 2$p_y$, 2$p_z$ basis functions. When this doubling of the minimal basis is done only for the valence orbitals one gets the Split Valence basis sets. For first row elements this gives 1$s$, 2$s$, 2$s’$, 2$p_x$, 2$p_y$, 2$p_z$ basis functions. Some well-known examples of split-valence basis functions are 3-21G. In this basis set, one contracted Gaussian of two primitives is used to represent each inner-shell atomic orbital. Each valence-shell orbital is represented by two functions, one a contracted Gaussian of two primitives and one a single primitive.

The Hartree-Fock theory has a limitation due to the use of the independent particle approximation where the instantaneous correlation of the motions of electrons is neglected. Neglecting the electron correlation will cause the difference between the exact energy and the Hartree-Fock energy to occur. This can be overcome by using one of the following ways: (i) configuration interaction (CI), (ii) Möller-Plesset perturbation theory [1], and (iii) Coupled-cluster theory [2].

The semi-empirical methods address the issue of limitations on calculations of large molecules and the length of computing time needed with ab initio methods. It does so by making several large assumptions, including ignoring core (non-valence) electrons and making major simplifications of the mathematics. Semi-empirical methods use many of the same mathematics as are found in the Hartree-Fock method, but look to reduce the computing time by replacing some of the mathematics with data (known as parameters) derived from experimental and computed data. The various types of semi-empirical methods use different numbers and types of parameters, which affect the quality of the calculation. The term semi-empirical comes from the fact that some of the calculations come from empirical data. Two simplest semi-empirical methods, i.e. Hückel and Pariser-Parr-Pople (PPP) are specifically for \pi-electron system or conjugated molecule [3].

In the Hückel method the matrix elements $[F_{ij}]$ are parameterized as follows:

$$F_{ij} = \begin{cases} \alpha; & \text{if } i = j \\ \beta; & \text{if } i \text{ and } j \text{ are nearest neighbors} \\ 0; & \text{else} \end{cases}$$

(12a)

where $\alpha$ is the negative of ionization potential of electrons from atomic orbital 2$p_z$ of carbon atoms and $\beta$ is its resonance energy. For a heteroatom (say X) which is bonded with a carbon atom, the values of $\alpha_x$ and $\beta_x$ are formulated as [5]:

$$\alpha_x = \alpha + h_x \beta; \quad \beta_x = k_x \beta$$

(12b)

The overlap integral is approximated as

$$S_{ij} = \delta_{ij} \text{ and } \sum_i c_{ni}^2 = 1$$

(13)

Using eq.s (12-13) one can solve the eq.s (8) with a non-iterative process.

Although the Hückel method can be used to predict the conjugated molecular properties, but this method cannot be used for electronic spectrum. This is caused by the neglect of electron-electron interactions. A better method for conjugated molecules is PPP method. The basic assumption in this method is differential overlap (ZDO), i.e.

$$\chi_i^{(\mu)}(\mu) \chi_j^{(\mu)}(\mu) = \chi_i^{(\mu)}(\mu) \chi_j^{(\mu)}(\mu) (14)$$

Applying ZDO, the overlap integral in eq. (6c) become $S_{ij} = \delta_{ij}$ and the two-electron integral in eq. (7c) become simple as

$$<ij(kl) = (ii)(kk) \delta_{ij} \delta_{kl} = \gamma_{i} \delta_{ij} \delta_{kl}$$

(15)

Therefore, the matrix elements $[F_{ij}]$ in eq. (7c) become

$$F_{ij} = H_{ij} + \gamma_{ij} P_{ij}$$

(16)

and

$$F_{ij} = \begin{cases} H_{ij} + \gamma_{ij} P_{ij}; & \text{if } i \text{ and } j \text{ are nearest neighbor} \\ 0; & \text{else} \end{cases}$$

with

$$H_{ij} = -I_i$$

(17)

$$H_{ij} = \beta = -2.5 \exp[(1.397 - r_{ij})/0.6]$$

where $r_{ij}$ is the bond length between carbon atoms $i$ and $j$, while

$$\gamma_{ij} = I_i - A_i$$

(18)
where \( I_1 \) and \( A_1 \) are the ionization potential and affinity of \( \pi \)-electrons respectively. The potential \( \gamma_0 \) is approximated using the Ohno formula,

\[
\gamma_0 = 11 \left( 1 + 0.584 r^2 \right)^{-1/2}
\] (19)

Some researchers have concluded that this method gives results which are deviated from experimental values. The deviations can be reduced by increasing the number of electrons involved in the calculation. There are some semi-empirical methods for valence electrons, but the Neglect of Diatomic Differential Overlap (NDDO) is the only model so far that really relates to an actual basis set. In this method, it was assumed that

\[
\chi_{IA}^*(\mu) \chi_{JB}^*(\mu) = \chi_{IA}^*(\mu) \chi_{IB}^*(\mu) \delta_{AB}
\] (20)

This leads to the following Fock matrix elements:

\[
F_{IAIA} = H_{IA} + \sum_{IA} P_{IAIA} \left[ \langle \{iA \} | | jA \rangle \right] \left( \frac{1}{2} \right) \left( \langle \{iA \} | | jA \rangle \right) \left( \frac{1}{2} \right) + \sum_{IB} P_{IAIB} \left[ \langle \{iA \} | | jB \rangle \right]
\]

\[
F_{IAIB} = H_{IA} + \sum_{IA} P_{IAIA} \left[ \langle \{iA \} | | jA \rangle \right] \left( \frac{1}{2} \right) \left( \langle \{iA \} | | jB \rangle \right) \left( \frac{1}{2} \right) \left( \langle \{iA \} | | jB \rangle \right) \left( \frac{1}{2} \right) + \sum_{IB} P_{IAIB} \left[ \langle \{iA \} | | jB \rangle \right]
\]

\[
F_{IBIB} = H_{IA} + \sum_{IB} P_{IAIB} \left[ \langle \{iB \} | | jB \rangle \right] \left( \frac{1}{2} \right) \left( \langle \{iB \} | | jB \rangle \right) \left( \frac{1}{2} \right) \left( \langle \{iB \} | | jB \rangle \right) \left( \frac{1}{2} \right) + \sum_{IB} P_{IBIB} \left[ \langle \{iB \} | | jB \rangle \right]
\]

However, it was until Dewar and coworkers [4] developed the modified neglect of differential overlap (MNDO) based on the NDDO formalism that latter became more widely used as predictive semi-empirical method. According to them, all two-electron two-center integrals involving charge clouds arising from pairs of orbitals on an atom were retained. The electron repulsion integrals are determined in terms of multipole-multipole interactions,

\[
\langle \{iA \} | | jB \rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=0}^{l} \sum_{l'=0}^{l} \frac{M_{lm} \left( l \right) M_{l'm} \left( l' \right)}{R_{AB}^{l+l'+2m+2}}
\] (21)

where the coefficients depends on \( l \), \( m \), and \( d_{lm} \) and the the multiple moment \( M_{lm} \) of charge distribution \( \rho (r, \theta, \phi) \) is defined by

\[
M_{lm} = \int d_{lm} r^l Y_l^m (\theta, \phi) \rho (r, \theta, \phi) d\tau
\] (22)

In this model the core-core repulsion term in energy was made as a function of the electron-electron repulsion integrals:

\[
E_{AB} = Z_A Z_B \left| s_A s_A \right| s_B s_B
\] (23)

where \( Z \) is the atomic number. The MNDO parameters are available for H, He, Li, Be, B, C, N, O, F, Al, Si, P, S, Cl, Zn, Ge, Br, Sn, I, Hg, and Pb.

The problem in the MNDO model is its inability to reproduce hydrogen bonding interactions due to a spurious repulsion at just outside chemical bonding distances. For that reason, Dewar et al. [6] developed AM1 (Austin Model 1) by modifying eq. (23) as follows:

\[
E_{AB} = Z_A Z_B \left| s_A s_A \right| s_B s_B
\]

\[
+ \frac{1}{R_{AB}} \sum_{i=1}^{n} d_{iA} e^{-\alpha_i (R_{AB} - \beta_i)} + d_{iB} e^{-\alpha_i (R_{AB} - \beta_i)}
\] (24)

In eq. (24), an atom has parameters \( a, b, \) and \( c \), each of them has four values. These parameters denote Gaussian functions that are centered at several distances to modifying the average potential between two atoms.

Stewart et al. [7] proposed Parameterization Model 3 (PM3) as a modification of AM1 model. They developed an optimization algorithm in the frame of Dewar’s NDDO. Simultaneously, they have optimized parameters for H, C, N, O, F, Al, Si, P, S, Cl, Br, and I. Now, MNDO, AM1 and PM3 are included together in a package called MOPAC.

**Applications**

1. **Ab initio**

The results of calculation by using GAMESS version with RHF/3-21G [10].

1.1 **Electronic structure of etene**

Number of atoms: 6; number of electrons: 16; number of basis set shell: 14; number of primitive basis functions: 26. For 16 electrons, number of occupied orbitals: 8.

Orbital energy:

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S</td>
<td>-11.1660</td>
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<tr>
<td>2S</td>
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<tr>
<td>3S</td>
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<tr>
<td>4S</td>
<td>-11.0385</td>
</tr>
<tr>
<td>5S</td>
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</tr>
<tr>
<td>6S</td>
<td>-11.0385</td>
</tr>
<tr>
<td>1P</td>
<td>-0.5903</td>
</tr>
<tr>
<td>2P</td>
<td>-0.5903</td>
</tr>
<tr>
<td>3P</td>
<td>-0.5903</td>
</tr>
<tr>
<td>4P</td>
<td>-0.5903</td>
</tr>
<tr>
<td>5P</td>
<td>-0.5903</td>
</tr>
<tr>
<td>6P</td>
<td>-0.5903</td>
</tr>
<tr>
<td>1D</td>
<td>0.3313</td>
</tr>
<tr>
<td>2D</td>
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<tr>
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</tr>
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<tr>
<td>2F</td>
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<tr>
<td>3F</td>
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<tr>
<td>4F</td>
<td>0.9272</td>
</tr>
<tr>
<td>5F</td>
<td>0.9272</td>
</tr>
<tr>
<td>6F</td>
<td>0.9272</td>
</tr>
</tbody>
</table>

Orbital energy:

-11.1316 eV, \( E_0 = 33.78 \) eV, \( E = 111.36 \) eV.

1B. **Electronic structure of butadiene**

Number of atoms: 10; number of electrons: 30; number of basis set shell: 48; number of primitive basis functions: 48. For 30 electrons, number of occupied orbitals: 15.

Orbital energy:

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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</tr>
<tr>
<td>4P</td>
<td>-0.5620</td>
</tr>
<tr>
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<td>6P</td>
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<td>0.3136</td>
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<td>2F</td>
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<td>0.3573</td>
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<tr>
<td>4F</td>
<td>0.3573</td>
</tr>
<tr>
<td>5F</td>
<td>0.3573</td>
</tr>
<tr>
<td>6F</td>
<td>0.3573</td>
</tr>
</tbody>
</table>

Orbital energy:

-154.06 eV, \( E_0 = 104.45 \) eV, \( E = -154.06 \) eV.
2. Semi-empiric

2A. Electronic structure of butadiene using Simple Hückel.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH}
\end{align*}
\]

From \( \det(F_{ij}-\varepsilon_{ij})=0 \), we get the following orbital energies and their orbital molecule:

\[
\begin{align*}
\varepsilon_1 &= \alpha - 1.62 \beta \\
\phi_1 &= 0.376 \chi_1 - 0.607 \chi_2 + 0.607 \chi_3 - 0.376 \chi_4 \\
\varepsilon_2 &= \alpha - 0.62 \beta \\
\phi_2 &= 0.607 \chi_1 - 0.376 \chi_2 - 0.376 \chi_3 + 0.607 \chi_4 \\
\varepsilon_3 &= \alpha + 0.62 \beta \\
\phi_3 &= 0.607 \chi_1 + 0.376 \chi_2 - 0.376 \chi_3 - 0.607 \chi_4 \\
\varepsilon_4 &= \alpha + 1.62 \beta \\
\phi_4 &= 0.376 \chi_1 + 0.607 \chi_2 + 0.607 \chi_3 + 0.376 \chi_4
\end{align*}
\]

From eq.(7b), we get the density matrix/bond order:

\[
\begin{align*}
p_{12} &= 2c_{11}c_{12} + 2c_{21}c_{22} = 0.912 \\
p_{23} &= 2c_{12}c_{13} + 2c_{22}c_{23} = 0.436 \\
p_{34} &= 2c_{13}c_{14} + 2c_{23}c_{24} = 0.912
\end{align*}
\]

These bond orders indicate that the middle bond is weaker and its corresponding bond length is longer than the two other bonds.

The free-valence of a carbon atom in a molecule determines the extent of susceptibility of that carbon atom to attack by free radicals [8]. The free-valence is approximated as

\[
V_i = 1.732 - \sum p_{ij}
\]

Using eq.s (26-27) we get the spectra as in Figure 2.

![Figure 1](image1.png)

**Figure 1** Butadiene along x-axis.

![Figure 2](image2.png)

**Figure 2** UV-Vis spectra of butadiene

2B. Absorption Spectra of butadiene using PPP

UV-Vis absorption along the x-axe of a molecule is given by

\[
A_{xx} = \sum_{m} \frac{\langle \Psi_{0} \mid \mu_{i} \mid \Psi_{m} \rangle \langle \Psi_{m} \mid \mu_{i} \mid \Psi_{0} \rangle}{\hbar(\omega_{m} - \omega - i\Gamma)}
\]

where \( \Psi_0 \) is the ground state and \( \Psi_m \equiv \Psi_n^{*} \) is an exited electronic state performed by the promotion of an electron from molecular orbital \( \varphi_n \) to \( \varphi_n^{*} \) with a singlet state of its spin function. The x-component of electric dipole moment is \( \mu_{i} = e\sum_{j} x_{j} \). Hence,

\[
\langle \Psi_{0} \mid \mu_{i} \mid \Psi_{m} \rangle = e \sum_{j} c_{ni} c_{nj} x_{j}
\]

where \( x_{j} \) is the position of the i-th carbon atom along the x-axis as in Figure 1.

2C. Effect of side groups on the HOMO-LUMO energy difference of phenylene vinylene

The following figures are phenylene vinylene (a) and one of its derivative (b).

![Figure 3](image3.png)

**Figure 3** Phenylene vinylene and one of its derivatives.

Using PPP method, we get the following orbital energies:

\[
\begin{align*}
\varepsilon_{a} (eV) &= -10.7492 -8.9742 -8.1338 -6.9683 -4.0317 -2.8662 -2.0258 -0.2508 \\
\Delta E_{a} &= 2.9366 eV \\
\varepsilon_{b} (eV) &= -11.0859 -9.4033 -8.9275 -7.5627 -4.5973 -3.4373 -2.0725 -1.5967 0.0859 \\
\Delta E_{b} &= 1.8054 eV
\end{align*}
\]

\( \Delta E_{b} < \Delta E_{a} \) means that the side group reduces the HOMO-LUMO energy difference. The UV-Vis of
those molecules are shown in Figure 3. We also see from those figures that the existence of side groups shifts the peaks to a longer wavelength or to a lower energy.

Phenylene vinylene is a monomer of poly-phenylene vinylene (PPV), the conjugated polymer that is useful for devices because it combine electrical and optical properties. The band gap of this polymer can be reduced if it is substituted with side groups such as methoxy ethyl hexyloxy (MEH) [9].

![Figure 3 UV-Vis spectra of (a) PV and (b) its derivative.](image)

**Figure 3** UV-Vis spectra of (a) PV and (b) its derivative.

2D. Electronic structure of phenylene vinylene and its derivative using MOPAC AM1

Phenylene vinylene: Number of occupied orbital: 20
Orbital energy (eV):
0.01919 0.55437 1.69214 3.08108 3.74465
3.89829 4.00776 4.11694 4.19113 4.46367
4.50252 4.78747 5.02090 5.14444 5.32257
5.45570 5.64622 5.69664 5.91682 6.10274
Ionization potential = 8.998 eV.

E_{el}= -4986.53 eV; E_n= 3853.15 eV, E_=- -1133.38 eV
Heat of formation = 161.59960 KJ.

Derivative of Phenylene vinylene:
Number of occupied orbital: 26
Orbital energy (eV):
-8.80558 0.05822 0.53362 1.73118 3.00798
3.78273 3.81738 3.99513 4.12440 4.13746
4.24218 4.42686 4.49705 4.53535 4.57910
4.67203 4.78396 4.85879 4.89607 5.19053
5.27585 5.38646 5.54547 5.72564 5.80564
5.98553 6.18119
Ionization potential: 8.81 eV.
E_{el}=7474.46 eV; E_n=6029.41 eV E_= -1445.05 eV.
Heat of formation = 103.96234 KJ.

We see that the side groups reduce the ionization potential and the heat of formation of phenylene vinylene.

**Conclusions**

The methodology of quantum chemistry of a many-electron system has been reviewed by showing the Hartree-Fock-Roothaan theory and its implementations for computations such as ab initio and semi-empirical methods. As the applications, ab initio method is applied for electronic structure of etene and butadiene using Games version. Simple Huckel and PPP methods are also used to show the electronic structure of butadiene, while the UV-Vis spectra of phenylene vinylene and its derivative is shown using PPP method. Finally, AM1 has been used to calculate the electronic structure, energy and heat of formation of phenylene vinylene and its derivative.

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**References**