

Green's functions in quantum chemistry II. Improving the Σ perturbation approach

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Abstract. Two methods, which are expected to lead to results better than those of the Σ perturbation approach given earlier are investigated. Within the algebraic approximation, the methods are applied to the hydrogen molecule and to ethylene in the Parisser-Parr-Pople (PPP) approximation. Both the methods are seen to suffer from the defect of not conserving the number of particles in the system. The methods are (a) the use of a partitioning other than Hartree-Fock. Due to the non-conservation of particle number, the method does not seem to be suited for the calculation of the ground state energy, but it gives good results for ionisation potentials. The investigation reveals that the only partitioning which conserves the number of particles is the Hartree-Fock partitioning (b) the renormalised Σ perturbation method, suggested by Csnak and others. For ethylene in the PPP approximation, the method does conserve the number of particles (but not in general). However, the energy obtained is not as good as that in the Σ perturbation method. This method therefore seems to be of limited applicability in molecular calculations.

Keywords. Green's functions; perturbation theory; electronic structure calculations.

1. Introduction

In an earlier paper (Sebastian 1978, hereafter referred to as I), we investigated the utility of the Σ perturbation method in molecular calculations. The method was found to be superior to the Hartree-Fock (HF) procedure in that it describes the dissociation of the hydrogen molecule correctly. The energy obtained was lower than that found by HF procedure. However, the improvement in energy was rather small, thus making the applicability of the method questionable, when compared with Configuration Interaction (CI) procedures. In this paper, we investigate two different methods for improving the results of I. Both methods make use of the Green's function (GF) formalism and have Dyson's equation, for the exact GF G , as their starting point.

$$G = G_0 + G_0 \Sigma G. \quad (1)$$

Here G_0 is the unperturbed propagator and Σ is the self energy operator. The two methods are essentially two different approximation procedures for the self energy and are based upon: (a) the use of a partitioning different from the commonly used HF partitioning (see below). (b) a renormalised Σ perturbation method—i.e. a diagrammatic series for Σ in terms of G .

Method A is applied to the hydrogen molecule and to ethylene while method B has been investigated for ethylene. (For ethylene, we work under the Pariser-Parr-Pople (PPP) approximation. For details of the PPP approximation the reader is referred to the excellent book by Salem (1966)). As our aim is an investigation of the utility of the two methods, we make use of a limited basis set—this being called the algebraic approximation (Wilson and Silver 1976)—consisting of four spin orbitals, denoted by $\phi_1(\mathbf{x})$, $\bar{\phi}_1(\mathbf{x})$, $\phi_2(\mathbf{x})$ and $\bar{\phi}_2(\mathbf{x})$ defined by

$$\begin{aligned}\phi_1(\mathbf{x}) &= \phi_1(\mathbf{r}) \alpha(\sigma) = [2(1+S)]^{-1/2} (\chi_1 + \chi_2) \alpha(\sigma), \\ \phi_2(\mathbf{x}) &= \phi_2(\mathbf{r}) \alpha(\sigma) = [2(1-S)]^{-1/2} (\chi_1 - \chi_2) \alpha(\sigma), \\ \bar{\phi}_1(\mathbf{x}) &= \phi_1(\mathbf{r}) \beta(\sigma), \\ \bar{\phi}_2(\mathbf{x}) &= \phi_2(\mathbf{r}) \beta(\sigma); \quad S = \langle \chi_1 | \chi_2 \rangle.\end{aligned}\quad (2)$$

Here $\mathbf{x} \equiv \mathbf{r}, \sigma$. χ_1 and χ_2 are atomic orbitals on the two atoms. For hydrogen molecule $\chi_1, \chi_2 = 1s$ orbital with an orbital exponent equal to unity; for ethylene $\chi_1, \chi_2 = 2p$ orbital on carbon. We adopt the following notations:

$$\begin{aligned}h_{ij} &= \langle \phi_i | h | \phi_j \rangle; \quad J_{ij} = \langle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) | (1/r_{12}) | \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \rangle \\ K_{ij} &= \langle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) | (1/r_{12}) | \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \rangle\end{aligned}\quad (3)$$

h being the one electron part of the Hamiltonian.

2. Method A. Use of a partitioning other than Hartree-Fock

The method of I was essentially a perturbation approach with the HF Hamiltonian as the unperturbed part. We expressed Σ as a perturbation series in terms of G_0 , the GF corresponding to the unperturbed Hamiltonian and the interaction. Approximating Σ by all terms, correct upto second order in the interaction is the procedure that was adopted in I (Σ_2 approximation). Because of the perturbation theoretical nature of the method, its results are strongly dependent on the energies of unoccupied orbitals. The HF method, as is well known, leads to very high values for the energies of virtual orbitals; these being much higher than the energies of particle states in the actual system. This must be the reason for the small improvement in total energy, observed in I. Consequently any method which makes the virtual orbitals correspond more closely to the actual orbitals is expected to lead to better results. Such a method has been proposed by Huzinaga *et al* (1973). In this section we apply the procedure of Huzinaga *et al* to the Σ perturbation method.

As the basic formalism of the Σ perturbation approach has been given earlier (Doll and Reinhardt 1972; Sebastian 1978), we will not reproduce it here. We write the Hamiltonian as

$$\begin{aligned}H &= \left\{ \sum_i [h(i) + V_{\text{eff}}(i)] \right\} + \left[\sum_{i < j} (1/r_{ij}) - \sum_i V_{\text{eff}}(i) \right], \\ &= H_0 + H^1.\end{aligned}\quad (4)$$

The eigenfunctions of $(h + V_{\text{eff}})$ will be denoted by ψ_n . Equation (4) with $V_{\text{eff}} = V_{\text{HF}}$ is the HF partitioning. Now we choose V_{eff} to be V_{HF} itself for the hole states while for the particle states it is different from V_{HF} . Thus we put

$$V_{\text{eff}} = V_{\text{HF}} + Q \Omega Q. \tag{5}$$

Q is the projection operator onto the particle states, defined by

$$Q = \sum_n^{\text{particle states}} |\psi_n\rangle \langle \psi_n|. \tag{6}$$

Ω is an operator which tries to compensate for the extra potential, felt by an electron in the particle states in the HF approximation. Different choices are possible for Ω . Huzinaga *et al* (1973) have given the physical reasoning behind the different choices.

In our scheme ϕ_2 and $\bar{\phi}_2$ are the only particle states. So we take

$$V_{\text{eff}} = V_{\text{HF}} + \Omega_0 [|\phi_2\rangle \langle \phi_2| + |\bar{\phi}_2\rangle \langle \bar{\phi}_2|]. \tag{7}$$

In the HF approximation, an electron in ϕ_2 would experience an extra field equal to $J_1 - K_1$, J_1 and K_1 being the usual coulomb and exchange operators of HF theory. To nullify the effect of this additional field, we put $\Omega_0 = -J_{12} + K_{12}$. With this choice of V_{eff} , the matrix representation of Σ in the basis $\phi_1, \phi_2, \bar{\phi}_1$ and $\bar{\phi}_2$ can be found, using the results of Doll and Reinhardt (1972). As Σ is spin independent, we get a block matrix with two identical blocks for each spin.

Thus for spin α ,

$$\Sigma = \begin{bmatrix} \frac{K_{12}^2}{(\omega + \epsilon_1 - 2\epsilon_2')} & 0 \\ 0 & -\Omega_0 + \frac{K_{12}^2}{(\omega + \epsilon_2' - 2\epsilon_1)} \end{bmatrix} \tag{8}$$

with $\epsilon_1 = h_{11} + J_{11}, \tag{9}$

and $\epsilon_2' = h_{22} + 2J_{12} - K_{12} + \Omega_0. \tag{10}$

(8), (9) and (1) lead to G^{-1} , the inverse of the matrix of G

$$G^{-1} = \begin{bmatrix} \omega - \epsilon_1 - \frac{K_{12}^2}{(\omega + \epsilon_1 - 2\epsilon_2')} & 0 \\ 0 & \omega - \epsilon_2 - \frac{K_{12}^2}{(\omega + \epsilon_2' - 2\epsilon_1)} \end{bmatrix} \tag{11}$$

Here $\epsilon_2 = h_{22} + 2J_{12} - K_{12}. \tag{12}$

The poles of G are now given by

$$\omega_1^\pm = \epsilon_2' \pm (\Delta^2 + K_{12}^2)^{\frac{1}{2}}, \quad (13)$$

and
$$\omega_2^\pm = \epsilon_1 - \Delta - \frac{\Omega_0}{2} \pm \left[\left(\Delta - \frac{\Omega_0}{2} \right)^2 + K_{12}^2 \right]^{\frac{1}{2}} \quad (14)$$

with
$$\Delta = \epsilon_2' - \epsilon_1. \quad (15)$$

The GF is now (see I)

$$G(\mathbf{x}, \mathbf{x}', \omega) = \sum_{\substack{i=1,2 \\ s=+,-}} \frac{g_i^s F_i(\mathbf{x}, \mathbf{x}')}{(\omega - \omega_i^s + i s \eta)}, \quad (16)$$

with
$$F_i(\mathbf{x}, \mathbf{x}') = \phi_i^*(\mathbf{x}) \phi_i(\mathbf{x}') + \bar{\phi}_i^*(\mathbf{x}) \bar{\phi}_i(\mathbf{x}'),$$

$$\eta = +0, \text{ and } g_1^- = \left[1 + \frac{K_{12}^2}{[\Delta + (\Delta^2 + K_{12}^2)^{\frac{1}{2}}]^2} \right]^{-1} \quad (17)$$

$$g_2^- = \left[1 + \frac{K_{12}^2}{\left\{ \Delta - \frac{\Omega_0}{2} - \sqrt{\left(\Delta - \frac{\Omega_0}{2} \right)^2 + K_{12}^2} \right\}^2} \right]^{-1} \quad (18)$$

The one-particle density matrix $\rho(\mathbf{x}, \mathbf{x}')$ and the ground state energy E_N^0 are now given by

$$\rho(\mathbf{x}, \mathbf{x}') = g_1^- F_1(\mathbf{x}, \mathbf{x}') + g_2^- F_2(\mathbf{x}, \mathbf{x}')$$

and
$$E_N^0 = g_1^- (h_{11} + \omega_1^-) + g_2^- (h_{22} + \omega_2^-) \quad (19)$$

2.1. Results

We have made calculations for the hydrogen molecule and the π -electron system of ethylene in the PPP approximation. The parameters used and the results are given in table 1. For purposes of comparison, we have reproduced the results of I. The results show the total energy to be considerably improved for ethylene while for hydrogen the improvement is small. However, as $g_1^- + g_2^-$ is found to be less than unity in both the cases, the one-electron density matrix is in error. Its trace, which must be equal to 2 is seen to be less than 2 for both systems; i.e., the method does not conserve the number of particles in the system. A similar problem occurs in the description of transport phenomena by approximate GF techniques (Kadanoff and Baym 1961; Baym 1962). For hydrogen in the large internuclear distance limit, both g_1^- and g_2^- approach 0.5 so that the number of particles is conserved in this limit. Also $E_N^0 \rightarrow 2 \langle \chi_1 | h | \chi_1 \rangle$, i.e. the dissociation of the molecule is described correctly. Due to non-conservation of particle number, the method, when applied to the calculation of binding energy would lead to a spurious dependence of the binding energy

on the position of the ' zero of the energy scale '. The non-conservation of particle number as well as the difference in results for the systems (results comparable to CI for ethylene while results are much inferior to CI for hydrogen) leads to the conclusion that the method is not suited for the calculation of ground state energy. Realising that ω_1^- corresponds to $E^{N,0} - E^{N-1,0}$, (see I), we have calculated $E^{N,0} - E^{N-1,0}$ using CI. The results are given in table 1. They show that ω_1^- calculated using the present approach is in better agreement with CI than the HF result or the result of I. So the method seems to be suited for the calculation of ionisation potentials and hence may be of use in the interpretation of photoelectron spectra. Noticing that

$$\left[1 + \frac{K_{12}^2}{[\Delta + (\Delta^2 + K_{12}^2)^{1/2}]^2} \right]^{-1} + \left[1 + \frac{K_{12}^2}{[\Delta - (\Delta^2 + K_{12}^2)^{1/2}]^2} \right]^{-1} = 1,$$

exactly and looking at (17) and (18), we conclude that the only possible choice of Ω_0 which will conserve the number of particles is $\Omega_0 = 0$ —i.e. the HF partitioning.

3. Method B. The renormalised Σ perturbation method

In this section, we investigate the renormalised Σ perturbation procedure, suggested by Csnak *et al* (1971). Eventhough the method was suggested in 1971, it does not seem to have been applied to molecular calculations. The method depends on the fact that diagrammatic summation techniques allow us to write Σ in terms of the exact GF, G as shown in (20). In (20), the double lines represent the exact GF. Equation (20) gives all the diagrams correct upto second order in the interaction

Table 1. Results for hydrogen molecule at $R=0.833\text{\AA}$ with an orbital exponent equal to unity and for the π -electron system of ethylene in the PPP approximation. For ethylene the values of parameters used were $\alpha=0.0$, $\beta=-2.371$, $\gamma_{11}=10.96$, $\gamma_{12}=6.895$.

	E_N^0 (eV)	g_1^-	g_2^-	$(g_1^- + g_2^-)$	ω_1^- (eV)	ω_2^- (eV)
(a) Hydrogen						
1. HF method	-1.6877	1.0	0.0	1.0	-0.5746	
2. Method of paper I	-1.7030	0.99933	6.7×10^{-4}	1.0	-0.5784	-3.3541
3. Method A of this paper	-1.7040	0.99749	0.00117	0.99866	-0.5818	-2.0157
4. CI using $c_1 \phi_1 \bar{\phi}_1 + c_2 \phi_2 \bar{\phi}_2 $	-1.7181	0.9808	0.0192	1.0	-0.5950	
(b) Ethylene						
1. HF method	4.1855	1.0	0.0	1.0	6.5565	
2. Method of paper I	3.9579	0.99246	0.00754	1.0	6.3803	-5.2567
3. Method A of this paper	3.6739	0.95961	0.01469	0.9643	6.1398	1.5661
4. CI using $c_1 \phi_1 \bar{\phi}_1 + c_2 \phi_2 \bar{\phi}_2 $	3.7683	0.94239	0.05761	1.0	6.1391	

$$\Sigma = \text{cloud with line} + \text{circle with line and wavy tail} + \text{cylinder with line} + \text{cloud with line} + \dots \quad (20)$$

(\Rightarrow $\equiv G$)

(Csnak *et al* 1971). Neglecting terms higher than first order in the interaction ($R\Sigma_1$ approximation), would lead to HF procedure. Thus $R\Sigma_1 \equiv \text{HF}$. We now approximate Σ by all terms correct upto second order in the interaction and call this $R\Sigma_2$ procedure. The $R\Sigma_2$ procedure takes into account a much larger class of diagrams than Σ_2 and hence is expected to lead to better results. It should be noted that (20) for Σ is based on the choice of the one-electron part of the Hamiltonian as the unperturbed part —i.e. $H_0 = \Sigma_i h(i)$ and G_0 now stands for the corresponding GF.

In the method *B* (and also in *A*), it is assumed that a finite basis set will be adequate to represent Σ and G . The use of a finite basis set leads to a simple structure for Σ (it has only poles) so that a simple iterative scheme may be employed in the numerical calculations pertaining to our applications. The procedure has the defect that it is incapable of reproducing the branch cuts which are present in the exact GF. However, arguments have been raised in favour of the assumption (Csnak *et al* 1971).

3.1. Application to ethylene

Under the algebraic approximation, the orbitals ϕ_1 and ϕ_2 are self-consistent solutions of the HF equations and have orbital energies ϵ_1 and ϵ_2 . We find it convenient to place the origin of the energy scale midway between the two, i.e. at $\epsilon_0 = \frac{1}{2}(\epsilon_1 + \epsilon_2)$. With this, the unperturbed propagator has poles at $h_{11} - \epsilon_0$ and $h_{22} - \epsilon_0$ and is given by

$$G_0(\mathbf{x}, \mathbf{x}', \omega) = \sum_{i=1,2} \frac{F_i(\mathbf{x}, \mathbf{x}')}{(\omega + \epsilon_0 - h_{ii})}. \quad (21)$$

Equation (1) may be written as

$$G^{-1} = G_0^{-1} - \Sigma. \quad (22)$$

In the $R\Sigma_2$ procedure, Σ itself is nonlinearly dependent on G , so that we have to adopt iterative methods for solving (22). Once G^{-1} is known, the poles of G can be found by expressing G^{-1} in a matrix form using the basis $\phi_1, \phi_2, \bar{\phi}_1$ and $\bar{\phi}_2$ and then calculating the values of ω at which the determinant of the matrix is zero. The symmetry of the system as well as the spin independence of Σ causes G^{-1} to be diagonal, so that for spin α , the poles of G are given by the solution of the algebraic equations

$$\omega - (h_{11} - \epsilon_0) - \Sigma_{11}(\omega) = 0, \quad (23a)$$

$$\omega - (h_{22} - \epsilon_0) - \Sigma_{22}(\omega) = 0, \quad (23b)$$

with exactly the same equations for spin β . As Σ_{ii} is dependent on ω , equations (23) will have, in general, more than one root. The roots will be denoted by ω_{ij}^s $i=1$ or 2 , $s=+$ or $-$ and j is allowed to take as many values as needed to specify all the poles of (23). $i=1(2)$ will denote that the pole arises from (23a) or (23b) (this notation is consistent with § 2, where it was not necessary to give values for j to specify all the poles) $s=+(-)$ that the root is positive (negative) (in § 2 this corresponds to the pole $>(<)\epsilon_0$). We assume that the poles have been arranged in the order of increasing magnitude i.e.

$$|\omega_{ij}^s| < |\omega_{ij+1}^s|.$$

The GF may now be written as

$$G(\mathbf{x}, \mathbf{x}', \omega) = \sum_{i=1,2} \frac{F_i(\mathbf{x}, \mathbf{x}')}{(\omega + \epsilon_0 - h_{ii} - \Sigma_{ii})} \quad (24)$$

Resolving into partial fractions, keeping in mind the position of poles of GF in the complex plane (see (17) of I), we get

$$G(\mathbf{x}, \mathbf{x}', \omega) = \sum_{\substack{i=1,2 \\ s=+,-}} \frac{g_{ij}^s F_i(\mathbf{x}, \mathbf{x}')}{(\omega - \omega_{ij}^s + is\eta)} \quad (25)$$

where g_{ij}^s determine the contribution of the pole at ω_{ij}^s to G and is given by

$$g_{ij}^s = \left[1 - \left(\frac{d\Sigma_{ii}(\omega)}{d\omega} \right) \omega_{ij}^s \right]^{-1}. \quad (26)$$

Solving self-consistently for G

Using (25), (23a) and (23b) become

$$\begin{aligned} \omega - (h_{11} - \epsilon_0) &= \left(\sum_j g_{1j}^- \right) J_{11} + \left(\sum_j g_{2j}^- \right) (2J_{12} - K_{12}) \\ &+ K_{12}^2 \sum_{ijk,s} \frac{g_{2i}^s g_{2j}^s g_{1k}^{-s}}{(\omega + \omega_{1k}^{-s} - \omega_{2i}^s - \omega_{2j}^s)} + 2(J_{12}^2 + K_{12}^2 - J_{12} K_{12}) \\ &\times \sum_{\substack{ik \\ s=+,-}} \frac{g_{1i}^s g_{2j}^s g_{2k}^{-s}}{(\omega + \omega_{2k}^{-s} - \omega_{1i}^s - \omega_{2j}^s)} \\ &+ J_{11}^2 \sum_{ijk,s} \frac{g_{1i}^s g_{1j}^s g_{1k}^{-s}}{(\omega + \omega_{1k}^{-s} - \omega_{1i}^s - \omega_{1j}^s)} \end{aligned} \quad (27a)$$

$$\begin{aligned}
\omega - (h_{22} - \epsilon_0) &= \left(\sum_j g_{2j}^- \right) J_{22} + \left(\sum_j g_{1j}^- \right) (2J_{12} - K_{12}) \\
&+ K_{12}^2 \sum_{ijk} \frac{g_{1i}^s g_{1j}^s g_{2k}^{-s}}{\left(\omega + \omega_{2k}^{-s} - \omega_{1i}^s - \omega_{1j}^s \right)} + 2(J_{12}^2 + K_{12}^2 - J_{12} K_{12}) \\
&\times \sum_{ijk} \frac{g_{2i}^s g_{1j}^s g_{1k}^{-s}}{\left(\omega + \omega_{1k}^{-s} - \omega_{2i}^s - \omega_{1j}^s \right)} \\
&+ J_{22}^2 \sum_{ijk} \frac{g_{2i}^s g_{2j}^s g_{2k}^{-s}}{\left(\omega + \omega_{2k}^{-s} - \omega_{2i}^s - \omega_{2j}^s \right)}. \tag{27b}
\end{aligned}$$

Equations (27) have to be solved self-consistently i.e. the ω_{ij}^s and g_{ij}^s have to be found in such a fashion that substitution of these quantities back in (27) and solving them, would lead to the same set of ω_{ij}^s and g_{ij}^s . The method that we adopt is as follows: The dominant terms of (27) are the ω -independent terms. Neglecting the other terms would lead to the HF equations. Now the ω -dependent terms may be considered as a small perturbation. So, the first step in our procedure is to find the HF results (step 0). Using these values for ω_{ij}^s and g_{ij}^s , (27) is set up and all the roots of (27) are found (step 1). For this, simple iterative procedures or the Newton-Raphson procedure may be used. Using the results of step 1 as input, (27) is again set up and solved (step 2) to get better values of ω_{ij}^s and g_{ij}^s . This is continued until self-consistency is achieved.

The numerical results for ethylene showed that in all steps the following equalities hold.

$$\omega_{2j, n}^{-s} = -\omega_{1j, n}^s, \tag{28}$$

$$g_{2j, n}^{-s} = g_{1j, n}^s, \tag{29}$$

$$\text{and } \sum_j g_{2j, n}^- + \sum_j g_{1j, n}^- = 1. \tag{30}$$

for $n = 0, 1, 2, 3, \dots$

(the additional subscript 'n' indicates that the quantity arose from the n th step). To prove the validity of (28) to (30), we assume them to hold for the results of n th step. Now consider the results of $(n+1)$ th step. Remembering that $J_{11} = J_{22}$ for ethylene in the PPP approximation, we see that (27b) in the $(n+1)$ th step can be obtained from (27a) by changing ω to $-\omega$. So if $\omega_{1j, n+1}^s$ is a solution of (27a),

then $-\omega_{1j, n+1}^s$ is a solution of (27b). Clearly, this root has to be denoted as $\omega_{2j, n+1}^{-s}$. Thus,

$$\omega_{2j, n+1}^{-s} = -\omega_{1j, n+1}^s, \tag{28a}$$

i.e. (28) is valid with n replaced by $(n+1)$. The validity of (29) for the $(n+1)$ th step is easily proved. Now consider

$$\begin{aligned} Z &= \sum_j g_{2j, n+1}^- + \sum_j g_{1j, n+1}^- \\ &= \sum_j g_{1j, n+1}^- + \sum_j g_{1j, n+1}^+, \end{aligned}$$

where (29) as applied to the $(n+1)$ th step has been made use of. Obviously,

$$\begin{aligned} Z &= \text{sum of all the residues of } (\omega - h_{11} + \epsilon_0 - \Sigma_{11, n})^{-1} \\ &= \text{negative of the residue at infinity,} \\ &= 1, \end{aligned}$$

because $\Sigma_{11, n}$ has the form

$$\Sigma_{11, n} = p + \sum_i \frac{q_i}{(\omega - r_i)},$$

p, q_i and r_i being constants.

Hence

$$\sum_j g_{2j, n+1}^- + \sum_j g_{1j, n+1}^- = 1. \tag{30a}$$

Now consider step 1. For this, the input is the HF results with $g_{11}^- = g_{21}^+ = 1, \omega_{11}^- = \epsilon_1 - \epsilon_0$ and $\omega_{21}^+ = \epsilon_2 - \epsilon_0$, all other g_{ij}^s being zero. This input satisfies (28), (29) and (30). Hence we conclude that (28), (29) and (30) must be valid for all values of n and hence for the final self-consistent result. After determining the self-consistent GF, we calculate the total energy E_N^0 and the one particle density matrix $\rho(\mathbf{x}, \mathbf{x}')$ to be

$$E_N^0 = \sum_j g_{1j}^- (h_{11} + \omega_{1j}^-) + \sum_j g_{2j}^- (h_{22} + \omega_{2j}^-), \tag{31}$$

$$\rho(\mathbf{x}, \mathbf{x}') = \sum_j g_{1j}^- F_1(\mathbf{x}, \mathbf{x}') + \sum_j g_{2j}^- F_2(\mathbf{x}, \mathbf{x}'). \tag{32}$$

The total number of electrons

$$\begin{aligned}
 N &= \int \rho(\mathbf{x}, \mathbf{x}) d\mathbf{x}, \\
 &= 2 \left(\sum_j g_{1j}^- + \sum_j g_{2j}^- \right), \\
 &= 2 \text{ because of (30)}.
 \end{aligned} \tag{33}$$

Thus for ethylene in the PPP approximation, the method gives correct answer for the number of particles. However, it should be noted that the proof of (33) is crucially dependent on (29), which in turn follows from the fact that (27b) can be obtained from (27a) by changing the sign of ω . But, in general $J_{11} \neq J_{22}$ and so (27b) cannot be obtained from (27a) by changing the sign of ω . On the left hand side of (30), the first sum is independent of J_{11} while the second is independent of J_{22} . So keeping J_{11} fixed and varying J_{22} will cause variations only in the first sum. This leads to the conclusion that, in general, (33) will not be satisfied, i.e. in general the $R\Sigma_2$ procedure does not conserve the number of particles.

4. Results

The results of our calculations on ethylene are given in table 2. The HF values are used as input for step 1. Step 1 leads to an increase in the number of poles—this occurs at each step of iteration. But poles which have very low value for g_{ij}^s ($\leq 10^{-7}$) will not make significant contribution to energy and the density matrix; so all such poles have been neglected. Iterations are continued until self-consistency is achieved. The results show that the improvement in energy is only 0.17 eV, compared with 0.23 eV for the Σ_2 approach. Further, the equations of $R\Sigma_2$ are much more complicated than those of Σ_2 .

Table 2. Calculations for the π -electron system of ethylene using method *B*. Parameters used are same as those given in table 1. The zero of the energy scale is taken to be at $\epsilon_0=12.375$. All energies are given in eV. For comparing results of table 2 with those of table 1, add 12.375 to all the energies of table 2. Step 0 gives HF results. Step 1, the results of Σ_2 approach. Self-consistency is arrived at after 6 steps. ω_{ij}^s and g_{ij}^s are given by the relations $\omega_{ij}^s = -\omega_{ji}^s$ and $g_{ij}^s = g_{ji}^s$. The results satisfy $\sum_j g_{ij}^- + \sum_j g_{ji}^- = 1$ exactly.

Step No.	0	1	2	6
ω_{12}^-			-29.6868	-29.8658
g_{12}^-			0.00275	1.7×10^{-5}
ω_{11}^-	-5.8185	-5.9946	-5.8701	-5.9394
g_{11}^-	1.0	0.99246	0.99022	0.99287
ω_{11}^+		17.6317	18.1523	17.9886
g_{11}^+		0.00754	0.00702	0.00711
ω_{12}^+			41.2582	41.9127
g_{12}^+			5.4×10^{-6}	4.3×10^{-6}
E_N^0	-8.1895	-8.4171	-8.3594	-8.3629

These results lead to the conclusion that the $R\Sigma_2$ approach is not suited for molecular electronic structure calculations.

5. Conclusions

Both the methods investigated in this paper have been found to have the defect of not conserving the particle number and hence are of limited applicability in the calculation of ground state energy. But method A seems to be suited for the calculation of ionisation potentials.

The investigation brings out an important point that is to be remembered when one uses an approximate GF technique for molecular calculations. The GFs should satisfy certain conservation laws. Thus the one-particle GF should satisfy the condition

$$\int [-iG(\mathbf{x}, \mathbf{x}, -0)] d\mathbf{x} = N.$$

Similar conditions have to be satisfied by the higher GFs. Calculations of total energy using approximate GFs exist in the literature (Toyoda *et al* 1975); *a priori* there does not seem to be any reason to suppose that the GFs used in this calculation will satisfy the conservation laws.

Thus it seems necessary to search for better perturbation procedures, which will conserve particle number and at the same time, give an energy comparable to CI.

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