

The scaled one-electron Hamiltonian model for open-shell LCAO-MO-SCF calculations: further corrections to the SOEH energy

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Abstract. The wavefunction generated by the scaled one-electron Hamiltonian (SOEH) model has been modified further by including all single excitations from the space of the SOEH function. A perturbation-variation ansatz has been invoked for obtaining the corresponding energy correction (ΔE_2). $[E(\text{SOEH}) + \Delta E_2]$ is shown to reproduce $E(\text{Roothaan})$ very closely. It has been demonstrated that by making ΔE_2 stationary with respect to change in μ , an approximate analytical expression for the theoretical calculation of the scaling parameter μ results. The corrected SOEH $[E(\text{SOEH}) + \Delta E_2]$ is shown to be quite useful for the calculation of geometrical parameters of open-shell systems even though it lacks the 'upper-boundedness' exhibited by $E(\text{SOEH})$.

Keywords. Open-shell SCF calculations; average Hamiltonian model; scaled one-electron Hamiltonian model; variation-perturbation calculation; second order energy correction.

1. Introduction

Recently, we have proposed a scaled one-electron Hamiltonian (SOEH) model for performing restricted open-shell calculations at an approximate level and tested its performance (Bhattacharyya 1981; Bhattacharyya and Chowdhury 1981; Banerjee and Bhattacharyya 1982). We may recall that the SOEH model belongs to the class of methods called the average Fock-operator models (Nesbet and Watson 1960; Nesbet 1961, 1963; Dewar *et al* 1968; Ellison and Matheu 1971; Carbo *et al* 1980) that have been suggested from time to time as expedient means of tackling the restricted open-shell Hartree-Fock problem for molecules in an approximate fashion. An evaluation of the performance pattern of our model (Banerjee and Bhattacharyya 1982) vis-a-vis that of the restricted open-shell method of Roothaan (1960) has shown that the SOEH model can be profitably utilised for structural investigations on open-shell molecular species at least at the semiempirical level of approximation (the method is yet to be tested in an *ab initio* framework). In fact, in all the cases investigated (Banerjee and Bhattacharyya 1982) the electronic energy calculated by the SOEH model was just slightly (0.005 a.u. on the average) above the energy calculated by Roothaan's procedure and thus appeared (was not demonstrated analytically) to have an upperbound character as it never shot below the energy calculated by the latter procedure. Needless to mention the energy estimated by the method of Roothaan itself is a variational upperbound to the exact energy.

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We may briefly recall here that the SOEH model operates by introducing a scaling parameter μ in the exchange part of the total energy in a Hartree-Fock like scheme, applying variational argument to the scaled pseudo-energy functional and, thereby generating a pseudo-Hartree-Fock like operator (F^{av}) which contains the scaling parameter (μ) explicitly as a multiplicative factor in the exchange operator (K_m) for the open-shell electron assigned to the orbital ϕ_m (say). In our previous studies we had interpreted μ as a mere averaging factor, the averaging process being applied to the exchange potential contributed by the closed- and the open-shell electrons. One may, however, look for an alternative rationalization of the parameter concerned. The present communication is a sequel to an afterthought of this kind. The strategy adopted for the projected investigation is straightforward. We use the orbitals generated by the SOEH model to construct the ground state wavefunction (ψ_0^{av}) and then modify this function by adding all single excitations from the doubly and singly occupied manifolds. The corresponding energy correction along with the amplitudes of various single excitations are determined by making use of a simple variation perturbation ansatz. The energy correction (ΔE_2) is an explicit as well as an implicit function of the scaling parameter μ . Accordingly making $\Delta E_2(\mu)$ stationary with respect to variation in the scaling parameter (i.e., by setting $\partial \Delta E_2 / \partial \mu = 0$), leads to an approximate analytical expression for μ (we call it μ_0). The energy correction ΔE_2 when added to the SOEH energy $E(\text{SOEH})$ (for a given scale factor μ) recovers, in most of the cases, the energy estimated by the RHF methodology of Roothaan (1960). But as ΔE_2 is not expected to have any 'upper-bound' character, the sum $[E(\text{SOEH}) + \Delta E_2]$ may even shoot below $E(\text{Roothaan})$ (see later). Even then we expect $[E(\text{SOEH}) + \Delta E_2]$ to remain very close to $E(\text{Roothaan})$, an expectation which is found to be correct in actual numerical calculations.

The outline of the paper is as follows. In §2 we develop our method and arrive at an analytical expression for ΔE_2 . We also attempt to rationalize the meaning of the μ parameter in the same context (§3). In §4.1 we have investigated the variation of $\Delta E_2(\mu)$, $[E(\text{SOEH}) + \Delta E_2]$ for various starting orbitals chosen. We may note here that the use of a specific value of μ in F^{av} determines a specific set of initial orbitals. The relative performances of $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2(\mu)]$ vis-a-vis $E(\text{Roothaan})$ in the calculation of geometrical features of a doublet radical in the ground state is discussed in §4.2 while §5 summarises the main findings of the present investigation.

2. Analytical expression for ΔE_2

Before setting out to derive an analytical expression for ΔE_2 we will first clarify our notations. The set $\{\phi_i\} i = 1, n_d$ represents the collection of doubly occupied orbitals, $\{\phi_m\} m = 1, n_o$, the singly occupied orbitals and $\{\phi_p\} p = 1, n_v$, the so-called virtual manifold, all generated by the SOEH (F^{av}) which contains the scaling-parameter μ . The corresponding eigenvalues are given by the sets $\{\epsilon_i\} i = 1, n_d$, $\{\epsilon_m\} m = 1, n_o$ and $\{\epsilon_p\} p = 1, n_v$ respectively. Let ψ_0^{av} represent the wavefunction for the doublet state of the open-shell system under consideration as envisaged in the SOEH model and let the 'corrected' wavefunction for the same state, after the inclusion of the 'specified' singly excited configurations (singly excited with respect to ψ_0^{av}) be $\tilde{\psi}_0$. Then (assuming a single open-shell orbital designated by ϕ_m) we have

$$\tilde{\psi}_0 = \psi_0^{\text{av}} + \sum_{i=1}^{n_d} C_{im} \psi_{im} + \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} C_{ip} \psi_{ip} + \sum_{p=1}^{n_v} C_{mp} \psi_{mp}, \quad (1)$$

where

$$\begin{aligned}\psi_0^{\text{av}} &= |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_i \dots \phi_m|; \psi_{im} = |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_m \dots \phi_m|; \\ \psi_{ip}(S=0) &= \frac{1}{\sqrt{2}} \{ |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_p \dots \phi_m| - |\phi_1 \bar{\phi}_1 \dots \bar{\phi}_i \phi_p \dots \phi_m| \}; \\ \psi_{mp} &= |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_i \dots \phi_p|;\end{aligned}$$

where $\psi_{ij}(S=0)$ merely denotes that the $\phi_i \rightarrow \phi_j$ excitation is a singlet spin-coupled one. One notes here in the passing that the configuration functions are built up from the orbitals generated by the SOEH model with a given value of μ .

Using $\tilde{\psi}_0$ defined by (1) as the trial wavefunction

$$E(\tilde{\psi}_0) = \langle \tilde{\psi}_0 | H | \tilde{\psi}_0 \rangle / \langle \tilde{\psi}_0 | \tilde{\psi}_0 \rangle. \quad (2)$$

Substituting (1) in (2) and retaining terms only upto the second order of magnitude, we have

$$\begin{aligned}E(\tilde{\psi}_0) &= E(\psi_0^{\text{av}}) + 2\mu \sum_{i=1}^{n_d} C_{im} \langle \phi_i \phi_m | \phi_m \phi_m \rangle \\ &+ \sum_{i=1}^{n_d} C_{im}^2 \{ \varepsilon_m - \varepsilon_i - J_{im} + \mu K_{mm} + (1 - \mu) K_{im} \} \\ &+ 2(\mu - 1) \sum_{p=1}^{n_v} C_{mp} \langle \phi_p \phi_m | \phi_m \phi_m \rangle \\ &+ \sum_{p=1}^{n_v} C_{mp}^2 \{ \varepsilon_p - \varepsilon_m - J_{mp} + \mu K_{mp} + (1 - \mu) K_{mm} \} \\ &+ 2\sqrt{2} (\mu - \frac{1}{2}) \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} C_{ip} \langle \phi_i \phi_m | \phi_p \phi_m \rangle \\ &+ \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} C_{ip}^2 \{ \varepsilon_p - \varepsilon_i - J_{ip} + 2K_{ip} - (\mu - \frac{1}{2}) K_{im} + (\mu - \frac{1}{2}) K_{pm} \}. \quad (3)\end{aligned}$$

To arrive at (3), use has been made of the fact that the orbitals used in the construction of all the configuration functions are eigenfunctions of the SOEH operator (F^{av}) where,

$$F^{\text{av}} = h(1) + \sum_{i=1}^{n_d} (2J_i - K_i) - J_m - \mu K_m. \quad (4)$$

In general, therefore, $F^{\text{av}} \phi_i = \varepsilon_i \phi_i$; where ϕ_i belongs to the doubly occupied, singly occupied or unoccupied manifolds. By way of clarifying the notations further, we may note here that

$$J_{ij} = \iint \phi_i(1) \phi_j(2) r_{12}^{-1} \phi_i(1) \phi_j(2) dv_1 dv_2$$

$$K_{ij} = \iint \phi_i(1) \phi_j(2) r_{12}^{-1} \phi_j(1) \phi_i(2) dv_1 dv_2,$$

and

$$\langle \phi_i \phi_j | \phi_k \phi_i \rangle = \iint \phi_i(1) \phi_j(2) r_{12}^{-1} \phi_k(1) \phi_i(2) dv_1 dv_2.$$

Now making the functional in (3) stationary with respect to various coefficients

appearing in (3) we arrive at

$$C_{im} = \frac{\mu \langle \phi_i \phi_m | \phi_m \phi_m \rangle}{\{\varepsilon_m - \varepsilon_i - J_{im} + K_{im}(1 - \mu) - \mu K_{mm}\}}, \tag{5}$$

$$C_{ip} = -\frac{\sqrt{2}(\mu - \frac{1}{2}) \langle \phi_i \phi_m | \phi_p \phi_m \rangle}{\{\varepsilon_p - \varepsilon_i + (\mu - \frac{1}{2}) K_{pm} - J_{ip} + 2K_{ip} + \frac{1}{2} K_{im}\}}, \tag{6}$$

$$C_{mp} = -\frac{(\mu - 1) \langle \phi_m \phi_m | \phi_m \phi_m \rangle}{\{\varepsilon_p - \varepsilon_m + \mu K_{mp} - J_{mp} - (\mu - 1) K_{mm}\}}. \tag{7}$$

Now substituting the values of the set of coefficients (C_{im}), (C_{ip}) and (C_{mp}) as given by (5) to (7) in (3), we arrive at the corrected expression for the SOEH energy after some trivial manipulations:

$$\begin{aligned} E(\tilde{\psi}_0) = E(\psi_0^{av}) - \mu^2 \sum_{i=1}^{n_d} \langle \phi_i \phi_m | \phi_m \phi_m \rangle^2 / \{\varepsilon_m - \varepsilon_i - J_{im} + (1 - \mu) K_{im} - \mu K_{mm}\} \\ - (\mu - 1)^2 \sum_{p=1}^{n_s} \langle \phi_m \phi_m | \phi_m \phi_p \rangle^2 / \{\varepsilon_p - \varepsilon_m + \mu K_{mp} - J_{mp} - (\mu - 1) K_{mm}\} \\ - 2(\mu - \frac{1}{2})^2 \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} \langle \phi_i \phi_m | \phi_p \phi_m \rangle^2 / \{\varepsilon_p - \varepsilon_i + (\mu - \frac{1}{2}) K_{pm} \\ + 2K_{ip} + \frac{1}{2} K_{im}\}. \end{aligned} \tag{8}$$

The correction to the SOEH energy, therefore turns out to be (at the level of approximation used by us) as follows

$$\Delta E_2 = E(\tilde{\psi}_0) - E(\psi_0^{av}) = -\mu^2 X - (\mu - 1)^2 Y - 2(\mu - \frac{1}{2})^2 Z \tag{9}$$

where

$$\begin{aligned} X &= \sum_{i=1}^{n_d} \langle \phi_i \phi_m | \phi_m \phi_m \rangle^2 / \{\varepsilon_m - \varepsilon_i - J_{im} + (1 - \mu) K_{im} - \mu K_{mm}\}, \\ Y &= \sum_{p=1}^{n_s} \langle \phi_m \phi_m | \phi_m \phi_p \rangle^2 / \{\varepsilon_p - \varepsilon_m + \mu K_{mp} - J_{mp} - (\mu - 1) K_{mm}\}, \\ Z &= \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} \langle \phi_i \phi_m | \phi_p \phi_m \rangle^2 / \{\varepsilon_p - \varepsilon_i + (\mu - \frac{1}{2}) K_{pm} + 2K_{ip} + \frac{1}{2} K_{im}\}. \end{aligned}$$

3. Approximate analytical expression for μ_0

We can write the corrected SOEH energy in the following series:

$$\begin{aligned} E &= (E_0 + \Delta E_1) + \Delta E_2 + \Delta E_3 + \dots \\ &= E(\text{SOEH}) + \Delta E_2 + \Delta E_3 + \dots \end{aligned} \tag{10}$$

Let us assume now that $E(\text{SOEH})$ has been calculated by using the values of μ obtained by brute-force optimization of $E(\text{SOEH})$ as a function of μ . So the $E(\text{SOEH})$ part of the energy series represented by (10) must be stationary with respect to further variation in μ . Hence, for this particular choice of reference point for the perturbation

expansion envisaged by (10), we have (upto 2nd order only)

$$\begin{aligned}\frac{\partial E}{\partial \mu} &= \frac{\partial E(\text{SOEH})}{\partial \mu} + \frac{\partial}{\partial \mu} (\Delta E_2) + \frac{\partial}{\partial \mu} (\Delta E_3) + \dots \\ &= 0 + \frac{\partial}{\partial \mu} \{ \Delta E_2 + \Delta E_3 + \dots \} \approx \frac{\partial}{\partial \mu} (\Delta E_2)\end{aligned}\quad (11)$$

assuming of course that the energy series in (10) converges. Hence, for the given choice of reference point the condition $\partial E/\partial \mu = 0$ is equivalent to demanding

$$\partial \Delta E_2 / \partial \mu = 0. \quad (12)$$

Since, ΔE_2 is given by (9), (12) leads us to,

$$\mu_0 = (Z + Y)/(X + Y + 2Z). \quad (13)$$

If we use some other reference energy [i.e., other than $E(\text{SOEH})$ calculated by $\mu = \mu_0$ (brute-force)] which is not far off from the optimum reference energy (13) still remains approximately valid. This is because the variation of $E(\text{SOEH})$ with μ (in the neighbourhood of $E(\text{SOEH})_{\text{optimum}}$) has been generally found to be very slow (Bhattacharyya 1981; Banerjee and Bhattacharyya 1982). Hence, setting $(\partial E/\partial \mu)(\text{SOEH}) = 0$ will be approximately valid even for non-optimum reference energy also. It may be mentioned here that a slightly better value of μ correct to second order could be estimated in principle by using (13) to calculate μ for a given set of starting orbitals, putting it back in F_{av} in (4) and iterating until a self-consistent value of μ is obtained. However, this would have increased the computational requirement considerably as many two-electron integrals would have to be recalculated at each SCF cycle. This SCF-perturbation approach was not therefore attempted by us.

A question to ponder over here is whether the μ_0 calculated by (13) should be identical with the μ_0 calculated by the brute-force optimization of $E(\text{SOEH})$ alone? The answer is clearly in the negative since $(\partial E/\partial \mu)(\text{SOEH}) = 0$ does *not* mean that higher order corrections (ΔE_2 , ΔE_3 etc.) are all zero. Thus, the present μ_0 corresponds to minimization of $[E(\text{SOEH}) + \Delta E_2]$ while the previous one was determined by the minimization of $E(\text{SOEH})$ alone. The two conditions are therefore not identical.

4. Results and discussion

4.1 Dependence of ΔE_2 on the choice of the starting orbitals

We have already noted at the outset that the scaling parameter μ occurs explicitly in the SOEH operator [viz, (4)] and therefore, different choices of μ will naturally generate different sets of initial orbitals for construction of the various configuration functions appearing in (1). It is therefore imperative to explore the μ -dependence of the calculated values of ΔE_2 as given by (9). In other words, this amounts to testing how sensitive the calculated values of ΔE_2 are to variations in the orbital basis-set used in the construction of the configuration functions in terms of which $\tilde{\psi}_0$ is expanded (1).

Table 1 summarises the results obtained for the 9 valence electron CN radical ($r_{\text{CN}} = 1.172 \text{ \AA}$) using the standard CNDO/2 parameters (Pople *et al* 1965). We have employed a wide range of values of μ (from 0.10 to 0.70 in steps of 0.05). In the present

Table 1. The pattern of variation of the SOEH energy and the corrected SOEH energy $[E(\text{SOEH}) + \Delta E_2]$ with changes of the scaling parameter μ observed for the ground state of the CN radical ($r_{\text{CN}} = 1.172 \text{ \AA}$)*. The calculated values of μ_0 are also reported.

Values of μ used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)	μ_0 (calculated)
0.10	-27.14544	-27.14549		0.2213
0.15	-27.14560	-27.14565		0.2215
0.20	-27.14579	-27.14583		0.2207
0.25	-27.14595	-27.14599		0.2199
0.30	-27.14607	-27.14611	-27.146363	0.2190
0.35	-27.14616	-27.14620		0.2181
0.40	-27.14622	-27.14627		0.2173
0.45	-27.14626	-27.14632		0.2165
0.50	-27.14628	-27.14635		0.2157
0.55	-27.14628	-27.146361		0.2149
0.60	-27.14624	-27.14633		0.2136
0.65	-27.14615	-27.14625		0.2124
0.70	-27.14605	-27.14616		0.2114

* Bond length from Sutton (1958).

case, the magnitude of ΔE_2 is very small but even then a 'soft' μ -dependence of ΔE_2 is discernible. One may notice further that while $E(\text{SOEH})$ as a function of μ shows up a flat minimum around $\mu = 0.50$ to 0.55 , the minimum of the modified SOEH energy i.e., the minimum of $[E(\text{SOEH}) + \Delta E_2]$ is a bit more prominent at $\mu = 0.55$. The minimum value of $[E(\text{SOEH}) + \Delta E_2] - 27.146361$ a.u. being admirably close to $E(\text{Roothaan})$ which is -27.146363 a.u. In this particular case neither $E(\text{SOEH})$ nor $[E(\text{SOEH}) + \Delta E_2]$ shoot below $E(\text{Roothaan})$. However, $[E(\text{SOEH}) + \Delta E_2]$ cannot, in general, be expected to show this kind of upperboundedness, as ΔE_2 is not bounded.

In table 1, we have also included the values of μ_0 calculated by using (13) for different sets of orbitals generated by F^{av} with different values of the scaling parameter μ . It is clear that the calculated values of μ_0 weakly depends on the choice of initial orbitals as revealed by the soft μ -dependence of the calculated value of μ_0 . One may note in this connection that our standard choice of $\mu = n_a/(n_a + n_p)$ leads to the value of $\mu = 0.5555$ in the present case while the μ_0 value predicted by our model turns out to be rather small ($\mu_0 = 0.21$). As mentioned earlier, this is expected as this possibly reflects the necessity of including still higher order excitations in (1) in order to predict reliable values of μ_0 . In other words the analytical structure of μ_0 appears to be far more involved than envisaged in the present model. The value of $[E(\text{SOEH}) + \Delta E_2]$ for $\mu = 0.5555$ is -27.14622 a.u., quite close to the value of $E(\text{Roothaan})$ (see table 1) which tends to suggest that in most of the cases $[E(\text{SOEH}) + \Delta E_2]$ corresponding to our standard choice μ will approximate $E(\text{Roothaan})$ sufficiently closely.

Table 2 summarises the results obtained for BF_2 (17 valence electrons, $\text{FBF} = 124.6^\circ$, $r_{\text{BF}} = 1.3 \text{ \AA}$) with μ varied in steps of 0.10 . In this case the minimum in $E(\text{SOEH})$ as a function of μ occurs at $\mu = 0.50$ while that in $[E(\text{SOEH}) + \Delta E_2]$ occurs at $\mu = 0.60$. However, $[E(\text{SOEH}) + \Delta E_2]$ shoots slightly below $E(\text{Roothaan})$ for the same species [$E(\text{Roothaan}) = -87.063522$ a.u., $(E(\text{SOEH}) + \Delta E_2)(\mu = 0.6) = -87.063547$ a.u.]. This as we have already discussed stems from the lack of 'upperboundedness' of ΔE_2 . In

Table 2. The pattern of μ -dependence displayed by $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ in $\text{BF}_2(r_{\text{BF}} = 1.3 \text{ \AA}, \text{F-B-F} = 124.6^\circ)^*$.

μ -values used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
0.0	-87.06303	-87.06313	
0.1	-87.06315	-87.06322	
0.2	-87.06329	-87.06334	
0.3	-87.06338	-87.06342	-87.063522
0.4	-87.06343	-87.06348	
0.5	-87.06345	-87.06352	
0.6	-87.06344	-87.06354	
0.7	-87.06333	-87.06348	

* Bond lengths and angles from Sutton (1958).

Table 3. The observed μ -dependence of $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ in $\text{NF}_2(r_{\text{NF}} = 1.35 \text{ \AA}, \text{F-N-F} = 139^\circ)^*$.

μ values used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
0.00	-106.77401	-106.77949	
0.05	-106.77395	-106.77835	
0.10	-106.77383	-106.77732	
0.15	-106.77361	-106.77642	
0.20	-106.77330	-106.77565	
0.25	-106.77289	-106.77499	-106.77402
0.30	-106.77239	-106.77445	
0.40	-106.77107	-106.77363	
0.50	-106.76937	-106.77317	
0.60	-106.76731	-106.77285	

* Bond lengths and angles from Sutton (1958).

contrast, $E(\text{SOEH})$ is seen to remain slightly above $E(\text{Roothaan})$ for any value of μ chosen by us revealing its upperbound character (Bhattacharyya and Chowdhury 1981; Banerjee and Bhattacharyya 1982).

In table 3 we have presented the rather interesting results obtained with NF_2 (19 valence electrons, $\text{FNF} = 139^\circ$, $r_{\text{NF}} = 1.35 \text{ \AA}$). The calculated values of ΔE_2 reveal in this case quite a perceptible μ -dependence. As can be seen from the table, ΔE_2 as a function of μ shows up a clear minimum at $\mu = 0.30$. On the other hand, $E(\text{SOEH})$ itself attains its minimum value for $\mu = 0.0$. Recalling that $E(\text{SOEH})$ represents the energy correct upto the first order, we would have expected ΔE_2 also to be minimum for $\mu = 0.0$. However, that demands that the energy series be convergent for $\mu = 0.0$. Possibly, for $\mu = 0.0$ the higher order terms begin to make sizable contribution, so that the truncation of the energy series at ΔE_2 may lead to erroneous conclusions. On the other hand, by setting $\mu = n_\alpha / (n_\alpha + n_\beta)$ for the present systems also, the SOEH energy, as seen from the table concerned, provides quite a good reference point for the calculation of the first correction to the SOEH energy.

4.2 Geometry optimization with $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$

Since the inclusion of ΔE_2 improves the energy estimate considerably in most of the systems studied, it would be worthwhile to test the effect of including ΔE_2 on the optimization of the geometrical parameters of simple radicals. Earlier, we have demonstrated (Banerjee and Bhattacharyya 1982) the utility of the 'native' SOEH model in the computation of equilibrium geometries of simple radicals or ions within the limits of approximate orbital theories. As a test case for our present study, we have chosen the HCO radical and we propose to optimize the H-C-O angle keeping r_{CH} and r_{CO} fixed at their experimental values (1.08 Å and 1.198 Å respectively).

Before proceeding to present results of geometry optimization of the HCO radical we will first discuss the results of a 'brute force' optimization of μ for H-C-O at a fixed geometry (viz, $r_{\text{CH}} = 1.08$ Å, $r_{\text{CO}} = 1.198$ Å, $\text{HCO} = 120^\circ$). The pertinent results are presented in table 4. One may easily see from the table concerned that both $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ attains minima for $\mu = 0.55$. We therefore used $\mu = 0.55$ in all our subsequent calculations pertaining to the optimization of the HCO angle in the HCO radical [note that $n_\alpha/(n_\alpha + n_\beta) = 0.5454$]. The results of these calculations are summarized in table 5. It is interesting to note that $[E(\text{SOEH}) + \Delta E_2]$ very closely reproduces $E(\text{Roothaan})$ for all the different values of $\theta(\text{H-C-O})$ studied by us. Also, except at $\theta(\text{H-C-O}) = 110^\circ$, $|E(\text{SOEH}) + \Delta E_2| < |E(\text{Roothaan})|$ for all other values of μ . Even for $\theta = 110^\circ$, $[E(\text{SOEH}) + \Delta E_2]$ only marginally shoots below $E(\text{Roothaan})$. For locating $\theta_{\text{min}}(\text{H-C-O})$ accurately, interpolation using cubic-splines was done with $E(\text{SOEH})$, $E(\text{Roothaan})$ and $[E(\text{SOEH}) + \Delta E_2]$ against θ . In all the cases θ_{min} turned out to be 133° (table 5). The final values of energy at θ_{min} estimated by the different methods have been given in table 5 for comparison. $[E(\text{SOEH}) + \Delta E_2]$ is found to be very close to $E(\text{Roothaan})$ at θ_{min} by lying slightly above the latter. $[E(\text{SOEH}) + \Delta E_2]$ can, therefore, be profitably utilised in geometry optimization as the estimation of ΔE_2 requires only a little effort. In fact, the total time required to compute the SOEH energy and the leading correction (ΔE_2) to it is approximately half the time required to calculate $E(\text{Roothaan})$ on the average. Further applications of this model for the calculation of equilibrium geometrical parameters of radicals are in progress and will be reported shortly. We would like to mention further that the method has been found to be applicable for the

Table 4. The observed μ -dependence of $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ in HCO radical ($r_{\text{CH}} = 1.08$ Å, $\text{H-C-O} = 120^\circ$, $r_{\text{CO}} = 1.198$ Å)*

μ -values used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
0.00	-25.87490	-25.87546	
0.40	-25.87810	-25.87848	
0.45	-25.87819	-25.87860	
0.50	-25.87824	-25.87869	-25.87942
0.55	-25.87826	-25.87877	
0.60	-25.87815	-25.87869	
0.65	-25.87802	-25.87863	
0.70	-25.87785	-25.87854	

* Bond lengths and angles from Sutton (1958).

Table 5. Variations in $E(\text{SOEH})$, $[E(\text{SOEH}) + \Delta E_2]$ and $E(\text{Roothaan})$ with changes in H-C-O angle of the HCO radical ($r_{\text{CH}} = 1.08 \text{ \AA}$, $r_{\text{CO}} = 1.198 \text{ \AA}$).

$\theta(\text{H-C-O})$ (degrees)	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
105	-25.86308	-25.86402	-25.86544
110	-25.86995	-25.87116	-25.87109
115	-25.87437	-25.87495	-25.87580
120	-25.87824	-25.87873	-25.87942
125	-25.88109	-25.88163	-25.88189
130	-25.88238	-25.88284	-25.88315
133	-25.88259	-25.88302	-25.88334
135	-25.88248	-25.88290	-25.88323
140	-25.88121	-25.88157	-25.88219
145	-25.87911	-25.87947	-25.88012
150	-25.87613	-25.87649	-25.87718

calculation of geometrical features of molecules in excited states (doublets and triplets). These results will be published in due course (Das and Bhattacharyya 1986).

5. Conclusions

The study reported in this paper has revealed a rather complicated analytical structure of the scaling parameter μ occurring in the SOEH model. The approximations used by us could only partially recover the optimum magnitude of the scaling parameter in different cases indicating the requirement for invoking a still higher order approximation for complete interpretation of the scaling parameter. However, the first or the leading correction (ΔE_2) to the SOEH energy has been found to be generally sufficient to reproduce $E(\text{Roothaan})$ very closely. The computational labour and cost is far less than is required for the calculation of $E(\text{Roothaan})$. Further generalization of the model appears to be necessary for a more complete understanding of the nature of the scaling parameter in the SOEH model.

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References

- Banerjee M and Bhattacharyya S P 1982 *Int. J. Quantum Chem.* **21** 905
 Bhattacharyya S P 1981 *Int. J. Quantum Chem.* **19** 735

- Bhattacharyya S P and Chowdhury M 1981 *Proc. Indian Acad. Sci. (Chem. Sci.)* **90** 391
- Carbo R, Dimingo L and Gregori J 1980 *Int. J. Quantum Chem.* **18** 1207
- Das K K and Bhattacharyya S P 1986 (to be communicated)
- Dewar M J S, Hashmall J A and Venier C J 1968 *J. Am. Chem. Soc.* **90** 1953
- Ellison F O and Matheu F M 1971 *Chem. Phys. Lett.* **10** 322
- Nesbet R K 1961 *Rev. Mod. Phys.* **33** 28
- Nesbet R K 1963 *Rev. Mod. Phys.* **35** 552
- Nesbet R K and Watson R E 1960 *Ann. Phys (N.Y.)* **9** 260
- Pople J A, Santry D P and Segal G A 1965 *J. Chem. Phys.* **43** S129, S136
- Roothaan C C J 1960 *Rev. Mod. Phys.* **32** 179
- Sutton L E 1958 in *Tables of interatomic distances and configurations in molecules and solids: spec. publ. No. 11* (London: The Chemical Society).