A Model Study of Instabilities Present in the Mean-Field Description and in Linearized Correlation Schemes

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In this work we discuss the cooperative occurrence of instabilities in the Hartree-Fock (HF) approximation and linearized correlation models. Both breakdown phenomena can be analyzed via eigenvalues of characteristic matrices. The well known HF instabilities follow from a quasi-degeneracy between the symmetry-adapted mean-field state and singly excited configurations. Quasi-degeneracies between the HF wave function and doubly excited configurations restrict the applicability of linearized correlation models. In the theoretical calculations the method of the local approach (LA) has been employed to derive the correlated ground state. For a system of the general topology XH_2 ($X = C$, Si, etc.) the bond orbital approximation (BOA) has been used to derive analytic formulae indicating the stability range of linearized correlation schemes. Numerical calculations on the basis of a simple model-Hamiltonian are given for the π systems C_2H_4 and C_2H_2, respectively, which have been studied as a function of the CC bondlength. The comparison of the respective numerical data indicates that both breakdown phenomena are enhanced via coupling terms between strongly correlated bonds.

1. Introduction

Investigations of the stability of the restricted Hartree-Fock (HF) wave function have a longer tradition in quantum chemistry. The HF instability conditions have been formulated by Thouless already in the early sixties [1]. Restricted HF wave functions $|\Phi_{\mathrm{SCF}}\rangle$ are locally unstable, if an additional energetic lowering is possible due to symmetry-breaking excitations of the single-particle type [2–4]. The stability of symmetry-adapted mean-field wave functions and physical consequences of symmetry-breaking have been analyzed by several authors in the past years [5–10]; the HF instability conditions are quite well documented in the literature.

Subsequently we will show that the mean-field instabilities occur cooperatively with breakdown phenomena (i.e. instabilities) of correlated wave functions $|\Psi_0\rangle$ when derived in terms of linearized approximations. Although possible nonanalytic solutions in linearized correlation models have been discussed by several authors [11–15] the strong interrelation between both instability conditions has not been mentioned until now.

In the present work we emphasize the cooperative occurrence of the mean-field instabilities and the breakdown of linearized correlation models. For the numerical calculations we have employed a simple semiempirical model-Hamiltonian of the INDO (intermediate neglect of differential overlap) type [16]. As we are not interested in the derivation of "exact" correlation energies this approximate LCAO model is sufficient for the scope of the subsequent analysis. The interatomic correlations have been determined by employing the method of the local approach (LA) [17–19]. In combination with simplified self-consistent-field (SCF) schemes this many-body formalism allowed for an efficient determination of the correlated ground state wave function $|\Psi_0\rangle$ [13, 20—26]. In previous realizations of the LA a linearized approximation has been adopted to evaluate $|\Psi_0\rangle$. In this degree of sophistication the LA has a pendant in the standard

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CEPA (coupled electron pair approximation) method [12, 27]. Subsequently we compare the results of the linearized LA realization with adaptations beyond the linearized approach. It will be shown that "many-body instabilities" (i.e. breakdown phenomena in the linearized description) are largely attenuated in the latter expansions.

As transparent model systems we have considered C_2H_4 and C_2H_2, respectively, which have been studied as a function of the CC bondlength. This comparative analysis allows to study the influence of coupling terms between strongly correlated bonds on the above (in)stability conditions. Furthermore we derive simple analytic formulae indicating the stability-range of linearized correlation models by using the bond orbital approximation (BOA) [28, 29]. For this purpose we have adopted a two-bond molecule with the general stoichiometry XH_2 ($X = C$, Si, Ge, etc.).

The outline of the present work is as follows. The conventional HF instability conditions for closed shell molecules as well as the theoretical background of the LA are presented in the next section. The model calculations for C_2H_4 and C_2H_2 are then summarized in Section 3. The analytic BOA formulae are derived in the subsequent part; final remarks are given in Section 5.

2. Theoretical Background

In the following only the most important aspects of the HF instability conditions are mentioned; for more detailed presentations see, e.g., [3–10]. For closed-shell molecules the HF instability condition is formulated by the eigenvalue problem

$$(A + B)\,C = \lambda^{\mathrm{HF}}\,C\,, \tag{2.1}$$

where the matrices A and B denote the mutual interaction between monoexcited configurations as well as between $|\Phi_{\mathrm{SCF}}\rangle$ and doubly excited states, respectively.

The restricted symmetry-adapted HF wave function is stable if the matrix $(A + B)$ is positive definite; i.e. if all eigenvalues are larger than zero. Roots $\lambda^{\mathrm{HF}} < 0$ can be either the result of an orbital degeneracy or can be produced via off-diagonal coupling terms in the HF instability problem [8, 30]. In order to quantify the symmetry-breaking character of the single-particle excitations in the HF instability problem the interaction matrices A and B are defined in terms of canonical MO's.

The theoretical basis of the LA in terms of a linearized approximation has been described in previous work [13, 17–22, 25]. The corrleated ground state $|\Psi_0\rangle$ is here written in the form

$$|\Psi_0\rangle = e^S\,|\Phi_{\mathrm{SCF}}\rangle \tag{2.2}$$

with

$$S = \sum_{IJ} \eta_{IJ}\,O_{IJ}\,. \tag{2.3}$$

The η_{IJ} in (2.3) are variational parameters and the O_{IJ} local projectors, allowing for the suppression of energetically unfavourable configurations in $|\Psi_0\rangle$ via two-particle excitations. In (2.3) capital letters are used to symbolize the localized regions I and J. We have employed the Foster-Boys method [31] to transform the canonical MO's from a conventional HF SCF calculation into a set of localized orbitals. The required local regions are then derived by projection of the localized orbitals on the different atoms and subsequent orthogonalization. The expressions

$$O'_{II} = n_{I\uparrow}\,n_{I\downarrow}\,, \tag{2.4}$$

$$O'_{IJ} = n_I\,n_J\,, \tag{2.5}$$

denote intrabond and interbond correlations of the density-density type in terms of local projection operators. In

$$O_{IJ} = O'_{IJ} - \langle O'_{IJ}\rangle\,, \tag{2.6}$$

the symbol $\langle\ldots\rangle$ has been used to abbreviate $\langle\Phi_{\mathrm{SCF}}|\ldots|\Phi_{\mathrm{SCF}}\rangle$. The density operators $n_I = \sum_\sigma n_{I\sigma}$ in (2.4) and (2.5) are associated to the electron density in the aforementioned local regions.

To calculate the correlated ground state $|\Psi_0\rangle$ we replace exp S by $1 + S$. The parameters η_{IJ} are then determined by minimization of

$$E = \langle\Psi_0|H|\Psi_0\rangle / \langle\Psi_0|\Psi_0\rangle. \tag{2.7}$$

A separate expansion of the numerator and denominator in (2.7) leads to

$$E^{\mathrm{den}}_{\mathrm{corr}} = E - \langle E\rangle = \frac{-2\sum_{IJ}\eta_{IJ}\langle O_{IJ}H\rangle + \sum_{IJKL}\eta_{IJ}\eta_{KL}\langle O_{IJ}HO_{KL}\rangle}{1 + \sum_{IJKL}\eta_{IJ}\eta_{KL}\langle O_{IJ}O_{KL}\rangle}\,. \tag{2.8}$$

for the interatomic correlation energy $E^{\mathrm{den}}_{\mathrm{corr}}$ in the "denominator variant" of the LA.

Expression (2.8) allows for the suppression of non-analytic solutions in the correlation energy which are encountered in the subsequently described linearized ansatz for the electronic correlations in the limit of quasi-degeneracy. The shortcoming of an evaluation via (2.8) is the well known size inconsistence in the calculated correlated ground-state wave function [27].

In the following we describe a linearized approximation for the determination of $|\Psi_0\rangle$. The electronic energy is here given by

$$E = \langle e^S | H | e^S \rangle_c . \qquad (2.9)$$

The index c indicates that the linked cluster theorem has been adopted to evaluate (2.9) [32]; i.e. only connected diagrams are taken into account when the expectation values are calculated. To solve (2.9), $\exp S$ is again replaced by $1+S$. This leads to

$$\sum_{KL} \langle O_{IJ}\, H O_{KL} \rangle_c\, \eta_{KL} = \langle O_{IJ}\, H \rangle_c , \qquad (2.10)$$

for η_{IJ} and to

$$E_{\text{corr}} = -\sum_{IJ} \eta_{IJ} \langle O_{IJ}\, H \rangle_c = \sum_n \varepsilon_n \qquad (2.11)$$

for the associated interatomic correlation energy E_{corr}.

It is seen that this approach requires the inversion of the matrix $\langle O_{IJ}\, H O_{KL} \rangle_c$. Therefore special care has to be taken when this matrix is singular. Singularities can be simply the result of operators that are linearly dependent. They decribe the same type of interatomic correlation processes. In this case it is a straightforward procedure to set the corresponding variational parameters η_{IJ} equal to zero. However, this situation must be discriminated from singular matrices $\langle O_{IJ}\, H O_{KL} \rangle_c$ which are a result of any geometric change in the molecule (i.e. elongation of a bondlength). Occurring singularities indicate now a quasi-degeneracy between $|\Phi_{\text{SCF}}\rangle$ and doubly excited configurations as a response to an external condition. For at least one "correlation channel" it is no longer possible to derive a gain in correlation energy via a virtual two-particle excitation. This type of singularity of $\langle O_{IJ}\, H O_{KL} \rangle_c$, coupled to an external variable (i.e. characteristic bondlength), will be discussed in the next two sections. To summarize; interaction matrices $\langle O_{IJ}\, H O_{KL} \rangle_c$ which are positive definite are the prerequisite for the calculation of physically reliable correlation energies.

It is thus convenient to define a many-body pendant to the HF instability problem (2.1).

The equation

$$\langle O_{IJ}\, H O_{KL} \rangle_c\, C_{\text{corr}} = \lambda^{\text{corr}}\, C_{\text{corr}} \qquad (2.12)$$

determines the stability of linearized correlation models via an energy balance between $|\Phi_{\text{SCF}}\rangle$ and doubly excited states. In (2.1) the corresponding roots λ^{HF} are determined via an energy balance between $|\Phi_{\text{SCF}}\rangle$ and singly excited configurations.

In addition to the denominator variant (2.8) for the correlated ground state and the linearized approximation (2.11) we have employed an expression which corresponds to a CEPA-1 type formulation of the LA. Detailed descriptions of the different CEPA variants for the correlated ground-state wave function can be found in [27, 33–36]. In

$$E - \langle H \rangle = -2 \sum_{ij}^{ab} \eta_{ij}^{ab} \langle Q_{ij}^{ab}\, H \rangle + \sum_{ij}^{ab} \sum_{kl}^{cd} \eta_{ij}^{ab}\, \eta_{kl}^{cd} \langle Q_{ij}^{ab} (H - A_{ij})\, Q_{kl}^{cd} \rangle \qquad (2.13)$$

we formulate the general CEPA equation which is of the same analytic structure as the basis equation of the LA. The energy-shift parameters A_{ij} in the present adaptation are defined in

$$A_{ij} = \sum_k (\varepsilon_{ik} + \varepsilon_{jk})/2 , \qquad (2.14)$$

in terms of pair-correlation energies

$$\varepsilon_{ij} = \sum_{ab} \eta_{ij}^{ab} \langle Q_{ij}^{ab}\, H \rangle . \qquad (2.15)$$

The Q_{ij}^{ab} in the above formula stand for excitation operators confined to doubly excited states. The associated indices i, j and a, b denote occupied and virtual canonical MO's. In the next section we have employed this CEPA-1 type realization of the LA to visualize the attenuation of nonanalytic solutions in the correlation energy due to the renormalization via the shift parameters A_{ij}. I.e. the terms $A_{ij} < 0$ guarantee positive definiteness of $\langle Q_{ij}^{ab} (H - A_{ij})\, Q_{kl}^{cd} \rangle$ also in the limit of stronger correlations. The correlation energies remain here rather wellbehaved. Nevertheless we show in the next section that smaller deviations from a regular behaviour are found in the region of the $\langle O_{IJ}\, H O_{KL} \rangle_c$ singularity.

3. Semiempirical Model Calculations of C_2H_4 and C_2H_2

In Table 1 we have summarized the results of the semiempirical model calculations of C_2H_4; the C_2H_2 data are given in Table 2. The employed INDO

Table 1. Correlation energy of C_2H_4 as a funcction of the $C=C$ bondlength $r_{C=C}$. The lowest roots of the HF singlet instability problem and the matrix $\langle O_{IJ}\, HO_{KL}\rangle_c$ are also given. E_{corr} has been calculated by CEPA-0 and CEPA-1 like methods in the LA and by the energy denominator version (E_{corr}, E_{corr}^{CEPA}, and E_{corr}^{den}, respectively). All energy values in eV, $r_{C=C}$ in Å; r_e = equilibrium bondlength.

$r_{C=C}$	E_{corr}	E_{corr}^{CEPA}	E_{corr}^{den}	λ^{corr}	λ^{HF}
r_e	−3.507	−3.367	−3.199	0.0142	7.57
1.55	−4.619	−4.066	−3.831	0.0107	4.45
1.75	−5.881	−4.629	−4.317	0.0416*	2.76
1.95	−8.269	−5.206	−4.769	0.0574*	1.28
2.15	−33.308	−5.768	−5.205	0.0133*	−0.13
2.20	+48.162	−5.887	−5.310	−0.0071	−0.47
2.25	+8.605	−6.043	−5.414	−0.0270	−0.80
2.30	+2.611	−6.177	−5.516	−0.0466	−1.13
2.50	−2.925	**	−5.909	−0.1224	−2.36

* Degenerate eigenvalues.
** No convergence in the iterative CEPA procedure.

Table 2. Correlation energy of C_2H_2 as a function of the $C\equiv C$ bondlength $r_{C\equiv C}$. The meaning of the different quantities is the same as in Table 1.

$r_{C\equiv C}$	E_{corr}	E_{corr}^{CEPA}	E_{corr}^{den}	λ^{corr}	λ^{HF}
r_e	−3.315	−3.273	−3.084	0.0508	3.23
1.31	−3.780	−3.711	−3.457	0.0737	2.49
1.41	−4.523	−4.378	−3.951	0.0505	0.20
1.46	−4.953	−4.642	−4.166	0.0601	−0.59
1.51	−5.494	−4.917	−4.363	0.0694	−1.20
1.56	−7.433	−5.221	−4.578	0.0344	−1.76
1.61	+5.467	−5.407	−4.731	−0.0079	−2.07
1.81	−5.409	**	−5.338	−0.1735	−3.32
2.01	−6.314	−6.293	−5.943	−0.3063	−4.31
2.21	−7.031	−7.030	−6.544	−0.4881	−5.12

** No convergence in the iterative CEPA procedure.

Hamiltonian has been described in [16]. In the present numerical adaptation the screened interaction of the original model has been replaced by bare "ab initio" potentials; see e.g. [20, 22, 25]. In the subsequent tables we have collected the interatomic correlation energy as derived in the linearized approximation (2.11), in the CEPA-1 pendant and the denominator results E_{corr}^{den} together with the lowest eigenvalues λ^{HF} and λ^{corr}, respectively, as a function of the CC bondlength.

The HF instability in C_2H_4 is predicted at 2.14 Å. The interaction matrix $\langle O_{IJ}\, HO_{KL}\rangle_c$ is here still positive definite. But a small elongation of the CC bondlength to 2.17 Å is sufficient to change the sign of λ^{corr}. The numerical data in Table 1 show clearly the nonanalytic behaviour of E_{corr} when $\langle O_{IJ}\, HO_{KL}\rangle_c$ becomes singular. E_{corr}^{den} and E_{corr}^{CEPA} remain rather wellbehaved. Smaller deviations from a simple analytic behaviour are nevertheless observed in the neighborhood of the $\langle O_{IJ}\, HO_{KL}\rangle_c$ singularity, indicating the breakdown of the linearized ansatz. This effect is discussed in some detail in connection with the C_2H_2 data.

A graphic representation of the interatomic correlation energy of C_2H_2 as a function of the $C\equiv C$ bondlength is given in Fig. 1; see also Table 2. In analogy to C_2H_4 the breakdown of the linearized correlation model follows the HF singlet instability. In C_2H_2 both "instabilities" have been predicted in a very narrow $r_{C=C}$ interval while an enlarged (spatial) difference between both critical points is found in C_2H_2. An analysis of the eigenvectors associated to λ^{HF} and λ^{corr} allows for a simple explanation of these differences. In C_2H_4 the most important interatomic correlations are taken into account in the LA. The HF instability in C_2H_2, however, is sizeably determined by fluctuations of the type $\pi_x \rightarrow \pi_y^*$ and $\pi_y \rightarrow \pi_x^*$. In the LA these correlation processes are not taken into account. But the neglect of certain correlation channels is accompanied by an attenuation of breakdown phenomena in the HF problem as well as linearized correlation schemes. In the next section this will be demonstrated in terms of a BOA analysis.

Figure 1 shows that the $\langle O_{IJ}\, HO_{KL}\rangle_c$ singularity is accompanied by a discontinuity in the CEPA-1 adaptation of the LA. Here it is possible to map E_{corr}^{CEPA} on the left- and right-hand side of the "forbidden" region via linear interpolations with different slopes. No convergent E_{corr}^{CEPA} solutions could be iterated up to convergence in the central region of Fig. 1 (bottom).

The results in the Tables 1 and 2 as well as Figure 1 can be summarized as follows. Although nonanalytic values of the correlation energy are suppressed in the CEPA-1 descendant of the LA due to the energy-shift parameters A_{IJ} a simple analytic continuation of E_{corr}^{CEPA} is not possible in the neighborhood of the $\langle O_{IJ}\, HO_{KL}\rangle_c$ singularity. The correlation energy E_{corr}^{CEPA} in the second "allowed $r_{C\equiv C}$ window" is smaller than extrapolated from shorter $r_{C\equiv C}$ distances. These effects (i.e. discontinuities) are strongly attenuated in the denominator variant, where E_{corr}^{den} remains highly analytic also in the vicinity of the breakdown of the linearized approximation.

The cooperative occurrence of the HF instabilities and the breakdown of linearized correlation schemes can be explained qualitatively in terms of simple

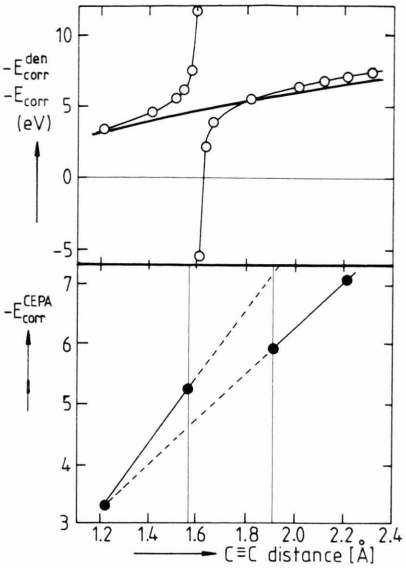

Fig. 1. Correlation energies in C_2H_2 as a function of the $C{\equiv}C$ bondlength. *Top:* E_{corr} (labelled by circles) and E_{corr}^{den} (bold line). *Bottom:* E_{corr}^{CEPA} in an enlarged energy scale. All energies in eV. In the central region (indicated in the display) no convergent CEPA solutions were feasible. In the geometric intervals left and right from this area we have indicated always the initial and final data points by circles. In both regions the correlation energy E_{corr}^{CEPA} can be mapped by straight lines with different slopes. The analytic continuations of both curves are indicated by broken lines.

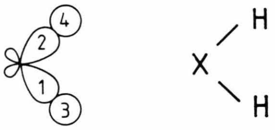

Fig. 2. Schematic representation of the local regions in XH_2. Each bond is defined via a hybrid at X (regions 1 and 2, respectively) and the 1 s AO (index 3 or 4) at the two hydrogen sites.

arguments. The HF instabilities accompanied by symmetry-breaking excitations indicate quasi-degeneracy between $|\Phi_{SCF}\rangle$ and singly excited configurations. But under these circumstances it is evident that one is also in the near neighborhood of a quasi-degeneracy between $|\Phi_{SCF}\rangle$ and doubly excited configurations; i.e. both types of instabilities occur cooperatively. The calculated correlation energy E_{corr} becomes here nonanalytical. The $\langle O_{IJ}\, HO_{KL}\rangle_c$ singularity additionally has a characteristic response in improved correlation models. By the consideration of additional operators in C_2H_2 it is possible to reduce the difference between the characteristic $r_{C\equiv C}$ values (i.e. instability points). Generally, breakdown phenomena are enhanced with increasing channels associated to strong electronic correlations. This problem is quantified in the next section and should be evident by comparing the C_2H_4 and C_2H_2 data.

In C_2H_4 only one strongly correlated π bond is found. The π_x/π_y interaction in C_2H_2 leads to additional channels for stronger electronic correlations limiting the stability-range of the HF approximation and linearized correlation models. As a consequence, the critical CC distances in C_2H_4 and C_2H_2 differ by more than 0.6 Å.

4. The Bond Orbital Approximation for the Correlated Ground State

In this section we use the BOA [28] to derive simple analytic expressions allowing to estimate the applicability of linearized correlation models; for recent BOA investigations we refer to [13, 21, 26, 29]. For the present analysis we have adopted a simple two-bond model XH_2 where only the correlations in and between the two $X-H\,\sigma$ bonds have been allowed; see Figure 2. Obviously this setup is also feasible to simulate the π_x/π_y correlations in C_2H_2.

In BOA it is assumed that the localized two-electron bonds do not interact with each other in the mean-field representation. The associated one-particle density matrices are block-diagonal with blocks of dimension 2×2. For the BOA mean-field state we have

$$|\Phi_{SCF}\rangle = \prod_{I\sigma} B_{I\sigma}^{+}\,|0\rangle\,, \tag{4.1}$$

where $B_{I\sigma}^{+}$ denotes the creation operator for an electron in the Ith bond; $|0\rangle$ is the vacuum state. In Figure 2 the different local regions of the XH_2 model are schematized. At X we have the two atomic hybrids 1 and 2, respectively. The local regions at the two hydrogen atoms are formed by the 1 s AO's 3 and 4. In BOA the expressions

$$B_{I\sigma}^{+} = \alpha\, b_{1\sigma}^{+} + (1-\alpha^2)^{1/2}\, b_{3\sigma}^{+}\,, \tag{4.2}$$

and

$$A_{I\sigma}^{+} = (1-\alpha^2)^{1/2}\, b_{1\sigma}^{+} - \alpha\, b_{3\sigma}^{+}\,, \tag{4.3}$$

are valid to express the bonding and antibonding linear combination of the Ith bond.

The operators $b_{i\sigma}^{+}$ create electrons with spin σ in the ith state. The parameter α in (4.2) and (4.3) is related to the bond polarity α_p in the corresponding localized bond via

$$\langle n_{1\sigma}\rangle = \alpha^2 = \tfrac{1}{2}(1+\alpha_p), \tag{4.4}$$

$$\langle n_{3\sigma}\rangle = 1-\alpha^2 = \tfrac{1}{2}(1-\alpha_p). \tag{4.5}$$

The value of α_p is determined by elements of the mean-field operator in the localized one-electron basis. We have

$$\alpha_p = T_F/(T_F^2 + T_0^2)^{1/2}, \tag{4.6}$$

with auxiliary parameters T_F and T_0 which are given by

$$2T_F = f_3 - f_1, \tag{4.7}$$

$$T_0 = t_0 + \tfrac{1}{2}(1-\alpha_p^2)^{1/2} V_{1133}. \tag{4.8}$$

T_F measures just the energy difference between the SCF states 1 and 3, respectively, and is identically equal to zero for homopolar bonds; the f_i in (4.7) are the elements of the Fock operator in the localized basis. T_0 in (4.8) is the conventional SCF hopping given by the bare hopping element t_0 (kinetic energy) and the two-electron interaction V_{1133}.

The BOA mean-field wave function (4.1) allows for a straightforward analytic formulation of the LA in the linearized approximation. In XH_2 we have one variational parameter η_0 describing the intrabond correlations, and one interbond element η_1. The associated projection operators are $O_1 = O_{11} = n_{1\uparrow} n_{1\downarrow}$ and $O_{12} = n_1 n_2$, respectively. The interatomic correlation energy $E_{\text{corr}}^{\text{BOA}}$ is then

$$\begin{aligned} E_{\text{corr}}^{\text{BOA}} = &-4\eta_0 \langle O_1 H\rangle_c + 2\eta_0^2 \langle O_1 H O_1\rangle_c \\ &-2\eta_1 \langle O_{12} H\rangle_c + \eta_1^2 \langle O_{12} H O_{12}\rangle_c \\ &+4\eta_0\eta_1 \langle O_1 H O_{12}\rangle_c . \end{aligned} \tag{4.9}$$

The matrix elements occurring in expression (4.9) are defined as

$$\langle O_1 H\rangle_c = \tfrac{1}{4}(1-\alpha_p^2)^2 V_0, \tag{4.10}$$

$$\langle O_1 H O_1\rangle_c = \tfrac{1}{4}(1-\alpha_p^2)^{3/2} t_0 F_0^{-1}, \tag{4.11}$$

$$\langle O_{12} H\rangle_c = (1-\alpha_p^2)^2 V_1, \tag{4.12}$$

$$\langle O_{12} H O_{12}\rangle_c = (1-\alpha_p^2)^{3/2} t_0 F_1^{-1}, \tag{4.13}$$

$$\langle O_1 H O_{12}\rangle_c = \tfrac{1}{4}(1-\alpha_p^2)^3 V_1 . \tag{4.14}$$

By adopting these expressions, the interatomic correlation energy $E_{\text{corr}}^{\text{BOA}}$ takes the form

$$\begin{aligned} E_{\text{corr}}^{\text{BOA}} = &-\eta_0(1-\alpha_p^2)^2 V_0 + \tfrac{1}{2}\eta_0^2(1-\alpha_p^2)^{3/2} t_0 F_0^{-1} \\ &-2\eta_1(1-\alpha_p^2)^2 V_1 + \eta_1^2(1-\alpha_p^2)^{3/2} t_0 F_1^{-1} \\ &+\eta_0\eta_1(1-\alpha_p^2)^3 V_1 . \end{aligned} \tag{4.15}$$

The abbreviations employed in (4.10) to (4.15) are explained below.

$$V_0 = \tfrac{1}{2}[\tfrac{1}{2}(V_{1111} + V_{3333}) - V_{1133}], \tag{4.16}$$

$$V_1 = \tfrac{1}{4}[(V_{1122} - \tfrac{1}{2}V_{1212}) + V_{3344} - 2V_{1144}], \tag{4.17}$$

$$F_0^{-1} = 1 + \alpha_p^2(1-\alpha_p^2)^{1/2}\frac{V_0}{t_0}, \tag{4.18}$$

$$F_1^{-1} = 1 + (1-\alpha_p^2)^{3/2}\frac{V_0}{2t_0} + \alpha_p^2(1-\alpha_p^2)^{1/2}\frac{V_1}{t_0}. \tag{4.19}$$

In F_0^{-1} and F_1^{-1} we have collected all elements leading to the difference between the present variational approach and conventional second order perturbation theory. Minimization of $E_{\text{corr}}^{\text{BOA}}$ leads to the following stationary values for the parameters η_0 and η_1:

$$\bar{\eta}_0 = (1-\alpha_p^2)^{1/2} F_0 \frac{V_0/t_0 - (1-\alpha_p^2)^{3/2}(V_1/t_0)^2 F_1}{1-\frac{1}{2}(1-\alpha_p^2)^3 (V_1/t_0)^2 F_0 F_1}, \tag{4.20}$$

$$\bar{\eta}_1 = (1-\alpha_p^2)^{1/2} F_1 \frac{1-\frac{1}{2}(1-\alpha_p^2)^{3/2}(V_0/t_0) F_0}{1-\frac{1}{2}(1-\alpha_p^2)^3 (V_1/t_0)^2 F_0 F_1}. \tag{4.21}$$

They both diverge if the denominator is equal to zero; i.e. when the matrix $\langle O_{IJ} H O_{KL}\rangle_c$ becomes singular. In this case $E_{\text{corr}}^{\text{BOA}}$ diverges too.

$$E_{\text{corr}}^{\text{BOA}} = -\bar{\eta}_0(1-\alpha_p^2)^2(V_0/2) - \bar{\eta}_1(1-\alpha_p^2)^2 V_1 . \tag{4.22}$$

The linearized variant of the LA breaks down if

$$1 = \tfrac{1}{2}(1-\alpha_p^2)^3 (V_1/t_0)^2 F_0 F_1 . \tag{4.23}$$

For a homopolar two-bond model the instability condition reads

$$V_1/t_0 = \sqrt{2 + V_0/t_0}. \tag{4.24}$$

For $V_1/t_0 > \sqrt{2+V_0/t_0}$ $E_{\text{corr}}^{\text{BOA}}$ does not correspond to a physically reliable minimum. From a formal point of view the instability in the linearized correlation model is a numerical response to the coupling between intra- and interbond correlations. With increasing bond-length r, the elements V_1 and t_0 differ in their decay properties. In V_1 the nonlocal Coulomb interactions (i.e. V_{1144} and V_{3344} in (4.17)) converge to zero for $r \to \infty$; the local interaction V_{1122}, however, remains constant. V_1 saturates consequently at a constant value for large internuclear separation r. With the decreasing to zero transfer integral t_0, one gets then condition (4.24) fulfilled at a certain value of r.

To illustrate this effect we give a simple numerical simulation for the XH_2 model. Thereby we adopt

Coulomb interactions of $V_{1111}=V_{1122}=15$ eV and $V_{3333}=24$ eV for C and H, respectively. For t_0 we take a value $t_{0e}=12$ eV at the supposed equilibrium bondlength of 1.1 Å; i.e. we have simulated the CH_2 case. The distance dependence of the corresponding matrix elements is approximated by

$$t_0 = t_{0e}\left(\frac{r_0}{r}\right)^{1.8}, \tag{4.25}$$

$$V_{1144} = C\Big/\sqrt{r^2+\frac{C^2}{4}(V_{1111}^{-1}+V_{3333}^{-1})^2}, \tag{4.26}$$

$$V_{3344} = C/\sqrt{3r^2+C^2 V_{3333}^{-2}}. \tag{4.27}$$

The interpolation for t_0 has been used in a recent BOA investigation where it proved to be of reliable accuracy [29]. (4.26) and (4.27) denote the Dewar-Sabelli-Ohno-Klopman (DSOK) [37] relation for the two nonlocal Coulomb expressions in V_1. The constant C in (4.26) and (4.27) amounts to 14.4 eV; the V_{iijj} are expressed in eV and r in Å. In our simple simulation we have assumed a constant H–X–H angle of 120°.

The results of the simple model calculation are schematized in Figure 3. As expected a nonanalytic behaviour in the interatomic correlation energy $E_{\text{corr}}^{\text{BOA}}$ is found for $\lambda_1^{\text{corr}}=0$. For the σ-type interaction in XH_2 we assume that the correlation energy is only realistic for r_{X-H} separations $r<2$ Å. Comparison with the numerical results in the last section shows that the breakdown of the linearized correlation model in the σ system is realized at larger bondlengths. In XH_2 we have $\lambda_1^{\text{corr}}=0$ for a X–H separation of ca. 2.8 Å. The explicit geometry characterizing the many-body instability depends obviously on the analytic details of the adopted matrix elements. Not the quantitative analysis, however, but the character of the dependence of $E_{\text{corr}}^{\text{BOA}}$ on a characteristic coordinate has been the purpose of the present simulation.

The BOA calculations have shown definitively, that "instabilities" in linearized correlation models have their origin in nonvanishing interbond coupling elements. The decisive influence of these parameters could be expected already on the basis of the semiempirical calculations of C_2H_4 and C_2H_2.

5. Conclusions

In the present investigation it has been shown for the first time that instabilities of the restricted mean-field ansatz and linearized correlation models occur cooperatively. The HF instabilities indicate a quasi-degeneracy between the symmetry-adapted mean-field ground state and symmetry-broken singly excited states. This quasi-degeneracy is accompanied by a second type of quasi-degeneracy, i.e. that between $|\Phi_{\text{SCF}}\rangle$ and doubly excited states. The latter condition leads to the breakdown of linearized correlation models. The relation between the HF and many-body instabilities is in so far of some relevance as the occurrence of HF instabilities can be employed as a diagnostic tool to estimate which type of correlation approach a system needs for its physically reliable treatment.

The BOA analysis of XH_2 has shown analytically that the breakdown of linearized correlation methods must be traced back to the coupling between intra- and interbond correlations. The same result has been verified numerically via the calculations of C_2H_4 and C_2H_2 which have indicated the enhanced breakdown phenomena with an increasing number of strongly correlated bonds.

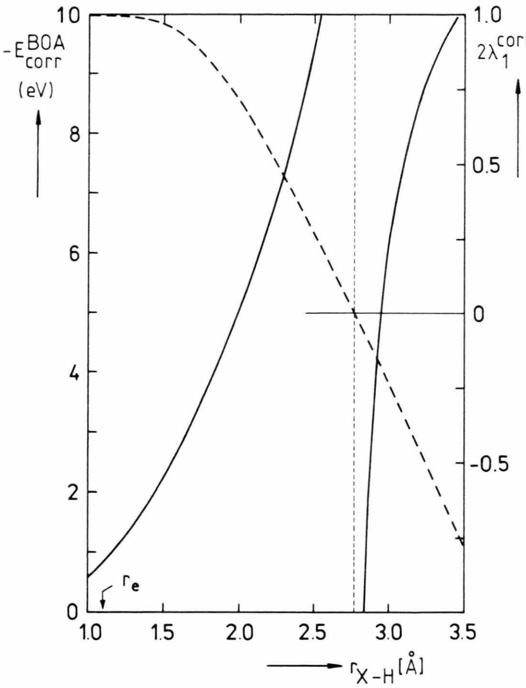

Fig. 3. Correlation energy $E_{\text{corr}}^{\text{BOA}}$ (solid line) and the lowest eigenvalue $2\lambda_1^{\text{corr}}/t_0$ of the $\langle O_{IJ}HO_{KL}\rangle_c$ matrix (dashed line) in XH_2 as a function of the X–H bondlength in the linearized LA. We have modelled CH_2. λ_1^{corr} has been normalized with respect to one half of the SCF hopping t_0.

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