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The Direct Determination of Brueckner Orbitals with Application to the H_2 Molecule*

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An iterative procedure is presented which allows for the direct determination of approximate Brueckner orbitals for small atomic and molecular systems. Starting from the Hartree-Fock determinant one first determines pair natural orbitals (PNOs) of independent electron pairs in the HF-field of the remaining electrons. The use of the generalized Brillouin-theorem then leads to an approximate Brueckner orbital for each electron pair. This procedure must be repeated up to self-consistency which is reached generally after 4–5 macroiterations. Applications to the ground state of H_2 show how important the use of Brueckner orbitals is to get good expectation values of one-electron operators and the correct asymptotic behaviour of the potential energy curve for large internuclear distances.

Es wird eine Iterationsmethode beschrieben, die eine direkte Bestimmung genäherter Brueckner-orbitale für kleine atomare und molekulare Systeme gestattet. Ausgehend von der Hartree-Fock-Determinante bestimmt man zunächst Paar-NOs (PNOs) der unabhängigen Elektronenpaare im HF-Feld der übrigen Elektronen des Systems. Mit Hilfe des verallgemeinerten Brillouin-Theorems erhält man dann ein genähertes Brucknerorbital für jedes Elektronenpaar. Dies Verfahren muß bis zur Selbstkonsistenz wiederholt werden, die man im allgemeinen nach 4–5 solcher Makroiterationen erreicht. Anwendung auf den Grundzustand des H_2-Moleküls zeigt, wie wichtig die Benutzung von Brucknerorbitalen ist, wenn man gute Erwartungswerte von Einelektronenoperatoren und das richtige asymptotische Verhalten der Potentialkurve bei großen Abständen erhalten will.

On propose un schéma itératif qui permet le calcul direct des orbitales de Brueckner approchées pour les atomes et les petites molécules. Partant du déterminant Hartree-Fock on calcule d'abord les PNO (pair natural orbitals) des paires indépendantes d'électrons dans le champ effectif des autres électrons dans l'approximation Hartree-Fock. Ensuite le théorème de Brillouin généralisé permet de calculer les orbitales de Brueckner approchées pour chaque paire d'electrons. On recommence le calcul des PNO, la "self-consistance" de cette méthode itérative s'établit en général au bout de 4 ou 5 macroitérations. Les applications à la molécule H_2 démontrent que l'utilisation d'orbitales de Brueckner s'impose si l'on s'intéresse à des bonnes valeurs moyennes d'opérateurs monoélectroniques ou au comportement asymptotique correct des courbes de potentiel aux grandes distances.

1. Introduction

The convenient starting point for a configuration interaction (CI) treatment of the electronic correlation in atoms and small molecules is a conventional restricted Hartree-Fock (HF) calculation, yielding the HF-determinant as a

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* Dedicated to the memory of Prof. K. H. Hansen.

reasonable leading configuration and an orthonormal set of occupied and virtual orbitals from which excited configurations – in the following we shall prefer the term "substituted configurations" – can be constructed.

The reason to choose this starting point for the CI-expansion is that the HF-determinant in many cases is already a good approximation to the wavefunction of the state under consideration. Only doubly substituted configurations (in the following abbreviated as DSC's) contribute largely to the correlation energy, since because of the Brillouin-theorem [1, 2] the energy contributions of the singly, triply, and higher substituted configurations vanish in first order. But the choice of the HF-determinant is unfavourable in two respects:

1. The coefficients of the singly substituted configurations (SSC's) do not vanish exactly, so that the HF-determinant despite of being the energetically best one-determinantal wavefunction has neither the best overlap with the true wavefunction of the system nor the best expectation values of one-electron operators obtainable with a one-determinantal wavefunction.

2. The HF-wavefunction is a rather poor approximation of the true one whenever it is degenerate or nearly degenerate with other configurations of the same symmetry, i.e. whenever the CI-expansion coefficients of one or more of the DSC's are comparable – in absolute value – to that of the HF-determinant. This happens, for instance, in many molecular systems at large internuclear distances; we only mention the well known example of H_2.

These deficiencies of the HF-determinant can be corrected by the inclusion of SSC's into the CI-expansion. Equivalently, one can start from the "best-overlap"- or "Brueckner"-determinant, constructed from the socalled "best-overlap" or "Brueckner-orbitals" (BO's) [3–8]. This choice of the leading configuration guarantees that the coefficients of the SSC's vanish identically [9], so that they need not to be included into the CI-expansion.

More familiar to quantum chemists are the "natural orbitals" (NO's) first introduced by Löwdin [10], which diagonalize the first order density matrix of the system. It has been noted that the BO's coincide with the first NO's in the case of two electrons [11, 12], but this holds only approximately for systems with more than two electrons [12, 13]. Whenever we are dealing with two electrons we shall use the terms "Brueckner orbitals" and "first NO's" synonymously.

Unfortunately, the determination of BO's and first NO's is much more complicated than the determination of the HF-orbitals. The reason is that because of the Brillouin-theorem [1, 2] the matrix elements of the Hamiltonian between the HF-determinant and the SSC's vanish. Therefore, the SSC's interact with the HF-determinant only indirectly via the DSC's, thus an expansion including SSC's and DSC's is necessary to determine the BO's.

The procedures proposed in the literature to construct BO's for atoms and molecules can be divided in two classes:

1. If very accurate wavefunctions of the state under consideration are known the BO's can be obtained according to the condition that the Brueckner-determinant has maximum overlap with the true wavefunction. But this method obviously is limited to systems for which sufficiently accurate wavefunctions are available and has been applied only to two-electron systems [11, 14–18] and to the Li-atom [12].

2. For the determination of BO's without knowledge of a very accurate wavefunction the conventional CI-expansions or MCSCF procedures are adequate provided that SSC's and DSC's are included simultaneously or that the leading configuration is reoptimized in the field of the DSC's. Of the latter type are the "extended Hartree-Fock" calculations of the Das and Wahl [19–21] yielding very good potential energy curves for H_2, Li_2, and F_2. Ahlrichs, Kutzelnigg, and Bingel [22] have calculated the first NO for the He-atom using a "macroiteration" scheme in which the "correlation potential" leading to the BO is taken into account iteratively. The same technique has been applied later by Kutzelnigg and Gélus [23] to calculate the valence shell correlation energy of Li_2 at large internuclear distances, but these authors run into difficulties with non-diagonal Lagrange multipliers if they want to include higher NO's of the same symmetry as the BO.

In this paper we present an alternative method for the direct determination of BO's avoiding this difficulty. The BO for a two-electron system is calculated in a macroiteration procedure using the generalized Brillouin-theorem [24] for MCSCF-wavefunctions. Each macroiteration cycle contains several microiterations to determine the higher NO's and the BO as described in Sect. 2a. For systems with more than two electrons we use the "independent electron pair approach" (IEPA) with step-by-step determination of "pair-NO's" or "pseudo-NO's" [25] for each individual pair in the HF-field of the remaining electrons as described by Ahlrichs and Kutzelnigg [26]. In this approximation we obtain a BO for each pair which should be called "pair-BO" or "pseudo-BO", analogously to the higher NO's. This procedure is similar to the one recently proposed by Larsson [18].

In Sect. 3 applications to the calculation of one-electron properties of H_2 at the equilibrium distance of 1.4 a_0 are presented. The errors of expectation values of some one-electron operators with the HF-determinant, Brueckner-determinant, and different CI-expansions are compared to the very accurate results of Kolos and Wolniewicz [27].

Sect. 4 contains results of the calculation of the potential energy curve of H_2 at large internuclear distances. A two-configuration wavefunction yields the correct asymptotic behaviour only if the first determinant is the Brueckner-determinant.

2. The Macroiteration Scheme to Determine Brueckner-Orbitals

a) The Ground State of a Two-Electron System

Let us first consider a two-electron system in its singlet ground state. Let φ_α, $\alpha = 1, 2 \ldots$, be a fixed set of orthonormal orbitals where φ_1 is the doubly occupied HF-orbital or an approximation to it.

The normalized wavefunction $\Psi(1,2)$ of the system can be expanded into a series of Slaterdeterminants

$$\Psi(1,2) = c_1 \Phi_1 + \sum_{\alpha > 1} c_\alpha \Phi_\alpha + \sum_{\alpha \geqq \beta > 1} c_{\alpha\beta} \Phi_{\alpha\beta} \tag{1}$$

where Φ_1 is the HF-determinant and Φ_α and $\Phi_{\alpha\beta}$ are singly and doubly substituted configurations (SSC's and DSC's, respectively):

$$\Phi_1 = |\varphi_1\bar{\varphi}_1| , \tag{2a}$$

$$\Phi_\alpha = \frac{1}{\sqrt{2}} \{|\varphi_1\bar{\varphi}_\alpha| + |\varphi_\alpha\bar{\varphi}_1|\} , \tag{2b}$$

$$\Phi_{\alpha\beta} = \frac{1}{\sqrt{2}} \{|\varphi_\alpha\bar{\varphi}_\beta| + |\varphi_\beta\bar{\varphi}_\alpha|\} . \tag{2c}$$

We shall assume for simplicity that the c_α, $c_{\alpha\beta}$ are real. The expectation value of an arbitrary operator $\boldsymbol{O}$ with respect to $\Psi(1,2)$ is then given by

$$\begin{aligned}(\Psi|\boldsymbol{O}|\Psi) = {} & c_1^2(\Phi_1|\boldsymbol{O}|\Phi_1) + 2c_1 \sum_\alpha c_\alpha(\Phi_1|\boldsymbol{O}|\Phi_\alpha) \\ & + 2c_1 \sum_{\alpha \geqq \beta} c_{\alpha\beta}(\Phi_1|\boldsymbol{O}|\Phi_{\alpha\beta}) + \sum_\alpha \sum_\gamma c_\alpha c_\gamma(\Phi_\alpha|\boldsymbol{O}|\Phi_\gamma) \\ & + \sum_{\alpha \geqq \beta} \sum_{\gamma \geqq \delta} c_{\alpha\beta} c_{\gamma\delta}(\Phi_{\alpha\beta}|\boldsymbol{O}|\Phi_{\gamma\delta}) \\ & + 2\sum_\alpha \sum_{\gamma \geqq \delta} c_\alpha c_{\gamma\delta}(\Phi_\alpha|\boldsymbol{O}|\Phi_{\gamma\delta}) .\end{aligned} \tag{3}$$

If $\boldsymbol{O}$ is a one-electron operator A, the terms $(\Phi_1|A|\Phi_{\alpha\beta})$ vanish. Further, if φ_1 is the HF-orbital and φ_α, $\alpha > 1$, orthogonal to it, as we have assumed, the Brillouin-theorem [1, 2] states that

$$(\Phi_1|\boldsymbol{H}|\Phi_\alpha) = 0 \quad \text{for all } \Phi_\alpha \tag{4}$$

and in most cases the coefficients c in (1) fulfill the relations

$$c_1 \approx 1; \qquad c_\alpha, c_{\alpha\beta} \ll 1 .$$

Actually, c_1, $c_{\alpha\beta}$ and c_α are of zeroth, first and second order, respectively, but here we are not concerned with a thorough discussion of the relative orders of magnitude of the terms appearing in (3), which has been given by Grimaldi [28].

With these simplifications the expectation values of A and $\boldsymbol{H}$ become

$$(\Psi|A|\Psi) = c_1^2(\Phi_1|A|\Phi_1) + 2c_1 \sum_\alpha c_\alpha(\Phi_1|A|\Phi_\alpha) + \cdots , \tag{5a}$$

$$(\Psi|\boldsymbol{H}|\Psi) = c_1^2(\Phi_1|\boldsymbol{H}|\Phi_1) + 2c_1 \sum_{\alpha \geqq \beta} c_{\alpha\beta}(\Phi_1|\boldsymbol{H}|\Phi_{\alpha\beta}) + \cdots . \tag{5b}$$

The terms represented by dots are identical to the last three terms in (3). Their overall contributions to the total expectation values are comparable to those of the terms linear in c_1.

The expressions (5a) and (5b) can be further simplified. If we know the coefficients c_α of the SSC's Φ_α, we can perform a linear transformation

$$\chi_1' = \mathcal{N}\left\{\varphi_1 + \frac{1}{\sqrt{2}c_1} \sum_\alpha c_\alpha \varphi_\alpha\right\} \tag{6}$$

where $\mathcal{N}$ is the normalization constant for the new orbital χ_1'. The Slater-determinant

$$\Phi_1' = |\chi_1'\bar{\chi}_1'| = \frac{\mathcal{N}^2}{c_1}\left\{c_1\Phi_1 + \sum_\alpha c_\alpha\Phi_\alpha + \frac{1}{\sqrt{2}c_1}\sum_{\alpha\geqq\beta} c_\alpha c_\beta\Phi_{\alpha\beta}\right\} \tag{7}$$

coincides with Ψ as far as Φ_1 and the SSC's are concerned. Φ_1' differs from Ψ only in the DSC's. This means, that on replacing Φ_1 by Φ_1' we get rid of the SSC's, or, stated differently, the choice of Φ_1' instead of Φ_1 makes the coefficients of the SSC's vanish. The wavefunction $\Psi(1,2)$ can now be written as

$$\begin{aligned}\Psi(1,2) &= \frac{c_1}{\mathcal{N}^2}\Phi_1' + \sum_{\alpha\geqq\beta}\left(c_{\alpha\beta} - \frac{c_\alpha c_\beta}{\sqrt{2}c_1}\right)\Phi_{\alpha\beta}\\ &= c_1'\Phi_1' + \sum_{\alpha\geqq\beta} c_{\alpha\beta}'\Phi_{\alpha\beta}\,.\end{aligned} \tag{8}$$

According to (6) the orbital χ_1' is not orthogonal to the φ_α, $\alpha > 1$, therefore the $\Phi_{\alpha\beta}$ in (8) are not orthogonal to Φ_1' and the expressions for the expectation values of $\boldsymbol{A}$ and $\boldsymbol{H}$ become more complicated. If we replace the virtual orbitals φ_α, $\alpha > 1$, by a new set φ_α', $\alpha > 1$, orthogonal to χ_1' and express the $\Phi_{\alpha\beta}$ in terms of these φ_α' we find still remaining SSC's

$$\Phi_\alpha' = \frac{1}{\sqrt{2}}\{|\chi_1'\bar{\varphi}_\alpha'| + |\varphi_\alpha'\bar{\chi}_1'|\}$$

with coefficients c_α' roughly proportional to $\sum_\beta c_{\alpha\beta}c_\beta$, i.e. generally much smaller than the original c_α.

Therefore, to construct the correct Brueckner orbital (BO) [3–8] χ_1 satisfying the Brueckner condition [9]

$$d_\alpha = \left(\Psi \,\middle|\, \frac{1}{\sqrt{2}}\{|\chi_1\bar{\chi}_\alpha| + |\chi_\alpha\bar{\chi}_1|\}\right) = 0 \quad \text{for all} \quad \alpha > 1 \tag{9}$$

(with the χ_α, $\alpha > 1$, orthogonal to χ_1) an iteration scheme is necessary:

Starting with φ_1, φ_α we determine χ_1' according to (6) and a set φ_α' orthogonal to χ_1'. Then we have to determine the new c_α' to perform the transformation (6) again and so forth.

In quite the same way – i.e. by changing the weakly occupied orbitals φ_α analogously to (6) – we can get rid of the "non-diagonal" coefficients $c_{\alpha\beta}$ with $\alpha \neq \beta$ and end up with the diagonal expansion

$$\Psi = d_1\Psi_1 + \sum_\alpha d_{\alpha\alpha}\Psi_{\alpha\alpha} = d_1|\chi_1\bar{\chi}_1| + \sum_\alpha d_{\alpha\alpha}|\chi_\alpha\bar{\chi}_\alpha|\,. \tag{10}$$

It is the well-known "natural expansion" of the wavefunction [29, 11], the orbitals χ_α are called "natural orbitals" (NO's) [10]. For the two-electron system the first NO χ_1 is identical to the Brueckner-orbital [11]. Wavefunctions of type (10) are nowadays often used in accurate ab-initio calculations because of their simplicity and rapid convergency.

The expectation values of A and H now read

$$(\Psi|A|\Psi) = d_1^2(\Psi_1|A|\Psi_1) + \sum_\alpha d_{\alpha\alpha}^2(\Psi_{\alpha\alpha}|A|\Psi_{\alpha\alpha}), \tag{11a}$$

$$\begin{aligned}(\Psi|H|\Psi) = d_1^2(\Psi_1|H|\Psi_1) &+ 2\sum_\alpha d_1 d_{\alpha\alpha}(\Psi_1|H|\Psi_{\alpha\alpha}) \\ &+ 2\sum_\alpha\sum_\beta d_{\alpha\alpha}d_{\beta\beta}(\Psi_{\alpha\alpha}|H|\Psi_{\beta\beta}).\end{aligned} \tag{11b}$$

Ψ_1 is the one-determinantal wavefunction giving the maximum overlap with Ψ and in most cases the best expectation values of one-electron operators (compare Sect. 3, [18]), but in view of the definition of the HF-orbital φ_1 it yields a poorer energy than Φ_1.

Now our problem is to calculate the coefficients c_α for a fixed set of orbitals φ_α in order to perform the transformation (6) from the MF-orbital to the first NO. This can be done with some different procedures, the conventional ones are:

a) Carry out a full configuration interaction with all SSC's Φ_α and all DSC's $\Phi_{\alpha\beta}$. Because of the Brillouin-theorem the SSC's do not contribute directly to the energy, thus, unfortunately, it is necessary to include all the DSC's, too.

b) Apply second order perturbation theory. Because of the Brillouin-theorem the first non-vanishing contribution to c_α is given by an expression like

$$c_\alpha = \sum_{\beta\gamma} \frac{(\Phi_1|H|\Phi_{\beta\gamma})(\Phi_{\beta\gamma}|H|\Phi_1)}{(E_1 - E_{\beta\gamma})(E_1 - E_\alpha)}. \tag{12}$$

E_1, E_α and $E_{\beta\gamma}$ are the energy expectation values of Φ_1, Φ_α and $\Phi_{\beta\gamma}$, respectively.

Both these methods are straightforward, but rather tedious, so we looked for a simpler, alternative procedure. The easiest way seems to use the generalized Brillouin-theorem [24] in connection with the NO-expansion (10). We shall describe this method in the following.

Again we start with a HF- or a near HF-solution φ_1. In the first step we calculate approximate NO's χ'_α, $\alpha > 1$, using the approximation $\chi_1 = \varphi_1$. We obtain an expansion

$$\Psi' = c_1|\varphi_1\bar{\varphi}_1| + \sum_\alpha d'_{\alpha\alpha}|\chi'_\alpha\bar{\chi}'_\alpha| \tag{13}$$

analogous to (10), but φ_1 still being the HF-orbital and χ'_α only approximate NO's. This first step is described explicitly by Ahlrichs and Kutzelnigg [26, 30], where one can find all the equations and formulae necessary for the calculation of the χ'_α and $d'_{\alpha\alpha}$.

The remaining error of the expansion (13) – provided that enough terms $|\chi'_\alpha\bar{\chi}'_\alpha|$ are included – comes from the approximation $\chi_1 = \varphi_1$. It can be corrected by the addition of SSC's. Let us for instance consider the SSC

$$\Phi_\lambda = \frac{1}{\sqrt{2}}\{|\varphi_1\bar{\varphi}_\lambda| + |\varphi_\lambda\bar{\varphi}_1|\} \tag{14}$$

with a trial orbital φ_λ, which is chosen to minimize the energy expectation value of the wavefunction

$$\Psi'' = c_1|\varphi_1\bar{\varphi}_1| + \sum_\alpha d'_{\alpha\alpha}|\chi'_\alpha\ \bar{\chi}'_\alpha| + c_\lambda\Phi_\lambda = \Psi' + c_\lambda\Phi_\lambda. \tag{15}$$

Obviously the addition of one single SSC Φ_λ is sufficient, because $c_\lambda \varphi_\lambda$ with optimized c_λ and φ_λ is completely equivalent to the sum $\sum_\alpha c_\alpha \varphi_\alpha$ with fixed φ_α entering into (6).

This is a variation problem for both c_λ and φ_λ, whereas c_1, $d'_{\alpha\alpha}$, φ_1, χ'_α remain fixed. The only constraint for the variation of φ_λ is that it must be orthogonal to φ_1. This problem is very similar to the HF-problem, and the easiest way to derive the variational equation for φ_λ is to use the generalized Brillouin-theorem [24]. It states – analogously to the common Brillouin-theorem in (4) – that the "optimal" orbital φ_λ fulfills the equation

$$(\Psi''|\boldsymbol{H}|\Psi''(\lambda\to\mu))=0 \tag{16}$$

for every φ_μ orthogonal to φ_1 and φ_λ.

In (16) $\Psi''(\lambda\to\mu)$ is the function derived from Ψ'' (15) by replacing φ_λ by φ_μ and dropping all determinants not containing φ_λ. Written explicitly the condition for φ_λ is

$$\begin{aligned}0&=(\Psi''|\boldsymbol{H}|\Psi''(\lambda\to\mu))\\&=\sqrt{2}c_1(h_{1\mu}+J^1_{1\mu})+\sqrt{2}\sum_\alpha d'_{\alpha\alpha}(h_{1\alpha}S_{\alpha\mu}+K^\alpha_{1\mu})\\&\quad+c_\lambda(h_{\lambda\mu}+J^1_{\lambda\mu}+K^1_{\lambda\mu})\\&=(\varphi_\mu\,|\,\sqrt{2}c_1(\boldsymbol{h}+\boldsymbol{J}^1)\,\varphi_1+\sqrt{2}\sum_\alpha d'_{\alpha\alpha}(\boldsymbol{K}^\alpha\varphi_1+h_{\alpha 1}\boldsymbol{S}\chi'_\alpha)\\&\quad+c_\lambda(\boldsymbol{h}+\boldsymbol{J}^1+\boldsymbol{K}^1)\varphi_\lambda)\end{aligned} \tag{17}$$

where $\boldsymbol{h}$ is the one-electron part of the Hamilton-operator, $\boldsymbol{S}$ the overlap matrix, $\boldsymbol{J}^i$ and $\boldsymbol{K}^i$ the Coulomb- and exchange operators of the orbital i, respectively. This condition can be fulfilled for any φ_μ only when φ_λ satisfies the following relation

$$\begin{aligned}&\sqrt{2}\left\{c_1(\boldsymbol{h}+\boldsymbol{J}^1)\,\varphi_1+\sum_\alpha d'_{\alpha\alpha}[\boldsymbol{K}^\alpha\varphi_1+h_{\alpha 1}\boldsymbol{S}\chi'_\alpha]\right\}\\&\qquad\qquad+c_\lambda(\boldsymbol{h}+\boldsymbol{J}^1+\boldsymbol{K}^1)\varphi_\lambda=\mu_\lambda\varphi_\lambda\,.\end{aligned} \tag{18}$$

This equation is very similar to the equation for the higher NO's χ'_α, but contains an inhomogeneous part not depending on φ_λ itself. For the solution of such inhomogeneous eigenvalue equations we use the method of Gabel [31], the explicit appearance of c_λ in (18) makes an iterative procedure necessary which is completely analogous to the iterative procedure for the construction of the approximate NO's themselves [26]. We shall call this type of iterations *microiterations.*

With the so determined c_λ and φ_λ we can perform the transformation

$$\chi'_1=\mathcal{N}\left\{\varphi_1+\frac{1}{\sqrt{2}c_1}c_\lambda\varphi_\lambda\right\} \tag{19}$$

from φ_1 to χ'_1 which is equivalent to (6). But according to the discussion following Eq. (8) this χ'_1 is not yet the correct BO. Similarly, the χ'_α are not yet the correct higher NO's, since they are determined with the approximation $\chi_1=\varphi_1$. Therefore, we have to use a *macroiteration* procedure: We start with $\chi_1^{(0)}=\varphi_1$, calculate the

$\chi_\alpha^{(0)}$ and $\varphi_\lambda^{(0)}$, perform the transformation (19) to construct a first approximation $\chi_1^{(1)}$ as described above. This $\chi_1^{(1)}$ is used to calculate better approximations $\chi_\alpha^{(1)}$ and $\varphi_\lambda^{(1)}$ for the higher NO's and so on. To reach self-consistency about 2–5 macroiterations are sufficient in our applications.

It is easy to see that our microiteration procedure for the determination of φ_λ and c_λ corresponds to an optimized fourth order perturbation method. Let us consider the typical fourth order energy contribution

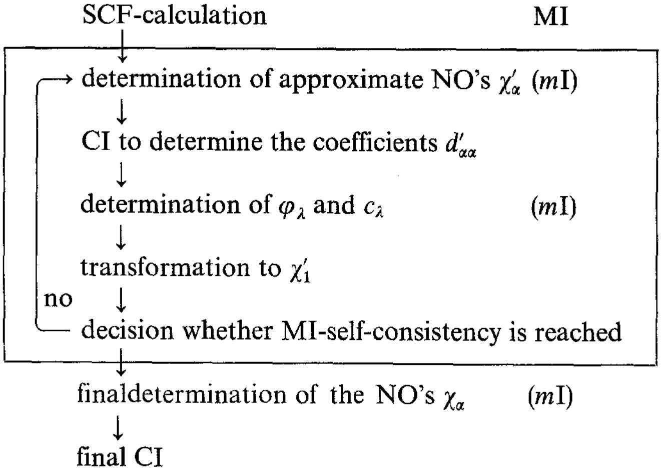
$$E_\lambda^{(4)} = \sum_{\beta\gamma}\sum_{\delta\varepsilon} \frac{(\Phi_1|H|\Phi_{\beta\gamma})(\Phi_{\beta\gamma}|H|\Phi_\lambda)(\Phi_\lambda|H|\Phi_{\delta\varepsilon})(\Phi_{\delta\varepsilon}|H|\Phi_1)}{(E_1-E_{\beta\gamma})(E_1-E_\lambda)(E_1-E_{\delta\varepsilon})} \tag{20}$$

and vary the orbital φ_λ occurring in the SSC Φ_λ to make $|E_\lambda^{(4)}|$ as large as possible. Using the abbreviations

$$c_{\beta\gamma} = \frac{(\Phi_1|H|\Phi_{\beta\gamma})}{E_1 - E_{\beta\gamma}}, \qquad c_{\delta\varepsilon} = \frac{(\Phi_1|H|\Phi_{\delta\varepsilon})}{E_1 - E_{\delta\varepsilon}} \tag{21}$$

for the terms in (20) not depending on φ_λ and noting that the orbital φ_λ as a linear combination of all the φ_α, $\alpha > 1$, cannot be orthogonal to the φ_α we get after some manipulations exactly formula (18) for the determination of φ_λ with the only trivial difference, that now also nondiagonal $c_{\beta\gamma}$ are occurring.

Our procedure can be summarized by the following floating diagram



mI means that for this step *micro*iterations are necessary while MI denotes the whole *macro*iteration block.

The advantage of this method seems to be that it is sufficient to determine only one single optimized function φ_λ instead of calculating all the c_α or instead of including all the SSC's into the CI in each MI-step. The determination of φ_λ and c_λ is very fast compared with the calculation of the matrix elements for the CI. In some cases it is possible to simplify the procedure in order to save computation time:

1. If all the $d'_{\alpha\alpha}$ in (13) are small compared with c_1 it is sufficient to determine φ_λ only once from (18), and to estimate c_λ and the energy contribution of Φ_λ per-

turbationally by

$$c_\lambda \approx \frac{(\Psi'|\boldsymbol{H}|\Phi_\lambda)}{E(\Psi') - E_\lambda}, \tag{22a}$$

$$\Delta E_\lambda \approx (\Psi'|\boldsymbol{H}|\Phi_\lambda) c_\lambda . \tag{22b}$$

The recalculation of better χ'_α, $d'_{\alpha\alpha}$ etc. does not change the results appreciably in that case (see, for instance, the equilibrium distance of H_2, Sect. 3).

2. Sometimes one can use a reduced basis throughout the whole MI-block. For instance, in H_2 at large internuclear separations only the second NO, which is of σ_u-type, has a large coefficient and must be included in the MI-procedure (Sect. 4). Therefore, we can limit ourselves to σ-type basis functions in the MI-block, the π-basis is necessary only for the final determination of all the NO's.

b) Closed Shell Systems with More than Two Electrons

Within the framework of the IEPA our procedure to construct first natural orbitals can be applied to closed shell systems with more than two electrons with slight modifications. Starting from the HF-determinant

$$\Phi_1 = |\varphi_1 \bar{\varphi}_1 \ldots \varphi_n \bar{\varphi}_n| \tag{23}$$

for a $2n$-electron system we pick out a pair of electrons occupying the same spatial orbital, say i. This pair can be treated completely analogous to the two-electron system in Sect. 2a, the only difference is that it now moves in the HF-field of the remaining electrons.

We shall not repeat all the details of the procedure, we only describe briefly the new points of view. Using the appropriate antisymmetrizer $\mathscr{A}$ we can split Φ_1 in the following way

$$\Phi_1 = \mathscr{A} |\varphi_i \bar{\varphi}_i| \cdot |\varphi_1 \bar{\varphi}_1 \ldots \bar{\varphi}_{i-1} \varphi_{i+1} \ldots \varphi_n \bar{\varphi}_n| \tag{24}$$

and replace the pair $|\varphi_i \bar{\varphi}_i|$ by an expansion of type (13)

$$|\varphi_i \bar{\varphi}_i| \rightarrow c_1^i |\varphi_i \bar{\varphi}_i| + \sum_\alpha d_{\alpha\alpha}^i |\chi_\alpha^i \bar{\chi}_\alpha^i| \tag{25}$$

the index i indicates that we are dealing with pair i. All the other pairs remain unchanged. The equation that determines the optimal φ_λ^i in the SSC

$$\Phi_\lambda^i = \frac{1}{\sqrt{2}} \{ |\varphi_i \bar{\varphi}_\lambda^i| + |\varphi_\lambda^i \bar{\varphi}_i| \} \tag{26}$$

now reads

$$\begin{aligned} \sqrt{2} \left\{ c_1^i (\boldsymbol{F}_i + \boldsymbol{J}^i) \varphi_i + \sum_\alpha d_{\alpha\alpha}^i [\boldsymbol{K}^\alpha \varphi_i + (\chi_\alpha^i | \boldsymbol{F}_i | \varphi_i) \boldsymbol{S} \chi_\alpha^i] \right\} & \\ + c_\lambda^i (\boldsymbol{F}_i + \boldsymbol{J}^i + \boldsymbol{K}^i) \varphi_\lambda^i = \mu_i \varphi_\lambda^i & \end{aligned} \tag{27}$$

with $$\boldsymbol{F}_i = \boldsymbol{h} + \sum_{j=1,n}^{j \neq i} (2\boldsymbol{J}^j - \boldsymbol{K}^j) . \tag{28}$$

This is completely analogous to (18), the only difference is the replacement of $\boldsymbol{h}$ by the effective one-electron potential $\boldsymbol{F}_i$. The solution of (27) involving micro- and macroiterations follows exactly the scheme described above for the solution of (18).

It must be noted that the NO's χ_α^i in (25) – including the first NO χ_1^i – are NO's of the pair i, but not of the whole system. That means, they only diagonalize the first order density matrix originating from the pair i in the HF-field of the remaining electrons of the system, but they do not diagonalize the total first order density matrix. These "pair-NO's" sometimes are called "pseudo-NO's" [25] or "quasi-NO's" [32]. In the same sense the χ_1^i are not the correct Brueckner-orbitals of the system, but "pair-Brueckner-orbitals", making vanish only that part of the SSC-coefficients c_α^i originating from DSC's in the same pair i. We are quite sure that this is the largest part of the c_α^i, but a thorough discussion of this question must be postponed and can be answered only in connection with the question of the additivity of pair-correlation energies in the IEPA. As we are dealing with an effective two-electron system, the "pair-Brueckner-orbitals" coincide with the first pair-NO's. Though this does not hold for the true orbitals [7], there is numerical evidence that they actually deviate very little from one-another [12].

This whole procedure can be carried through for each individual pair $i = 1, \ldots, n$. But here one more step is necessary: One has to take into account that after the transformation from φ_i to χ_1^i the field in which the remaining electrons are moving has changed, too. To reach self-consistency we therefore need a still higher level of macroiterations: One starts, for instance, with the construction of χ_1^1 in the HF-field of all the other pairs, continues with the construction of χ_1^2 in the field of $\chi_1^1, \varphi_3, \ldots, \varphi_n$, and so on to χ_1^n. Then one corrects χ_1^1, now in the field of the just determined $\chi_1^2, \ldots, \chi_1^n$, and so on up to self-consistency.

3. Expectation Values of One-Electron Operators. The Quadrupole Moment and Field Gradient of H_2

As a first example of the application of our macroiteration procedure we have calculated the energy and the expectation values of some one-electron operators for the H_2-molecule at its equilibrium distance.

We start from a wavefunction as described in (13), i.e. from a CI-function containing the SCF-determinant Φ_1 and all the DSC's (or a sufficiently large number of them), but which does not include the SSC's. According to Sect. 2 functions of this type generally give good expectation values for the Hamiltonian, since the SSC's neglected in (13) have a priori vanishing matrix elements with Φ_1. But this does not hold for other operators.

Therefore, to get as accurate results for the expectation values of one-electron operators as for the Hamiltonian we must include the SSC's or, equivalently, use the full diagonal expansion (10). Such a wavefunction will give a slightly better value for the energy, too, for now the matrix elements of the type (SSC$|\boldsymbol{H}|$DSC) are also taken into account. How to construct the full diagonal expansion was shown in Sect. 2.

For the calculation of H_2 at its equilibrium distance we used an extended Hoyland-type basis [33] of 45 Gaussian lobe functions contracted to 23 groups (11σ-type, 5π-type and one δ-type for both components). This medium-sized basis

Table 1. CI-function for H_2 before and after the MI treatment (equilibrium distance)

No.	Configurations	Before MI Coefficient	Energy contribution	After MI Coefficient	Energy contribution
1	$\sigma_g\bar{\sigma}_g$	0.99086	-1.133095^a	0.99086	-1.132977^a
2	$\sigma_u\bar{\sigma}_u$	-0.10076	-0.016717	-0.10164	-0.017043
3	$\sigma_g\bar{\sigma}_g$	-0.05533	-0.007429	-0.05474	-0.007355
4, 5	$\pi_u\bar{\pi}_u$	-0.04666	-0.005310	-0.04645	-0.005289
6	$\sigma_u\bar{\sigma}_u$	-0.01039	-0.000763	-0.01047	-0.000776
7	$\sigma_g\bar{\sigma}_g$	-0.00974	-0.000720	-0.00983	-0.000733
8, 9	$\pi_g\bar{\pi}_g$	-0.00842	-0.000499	-0.00844	-0.000504
0,11	$\delta_g\bar{\delta}_g$	-0.00646	-0.000299	-0.00642	-0.000296
12	$\sigma_g\bar{\sigma}_g$	-0.00645	-0.000338	-0.00641	-0.000335
13, 14	$\pi_u\bar{\pi}_u$	-0.00606	-0.000290	-0.00604	-0.000289
15	Φ_λ	0.00959	-0.000112	0.00000_5	0.000000
E_{tktol}			-1.171970		-1.171973

[a] All energies in atomic units (a.u.).

should allow for rather good results. Thus, our SCF-energy is about 0.0005 a.u., our correlation energy about 0.0019 a.u. poorer than the very accurate results of Kolos and Roothaan [34].

In Table 1 the results of the calculation of the total energy are summarized. For each configuration we tabulated the expansion coefficient and the energy contribution obtained 1) with the wavefunction (13) augmented by one optimized configuration Φ_λ and 2) after the complete MI-procedure (3 macroiterations were necessary to reach self-consistency to 7 figures in energy). The first configuration is the SCF-determinant (after MI of course the Brueckner-determinant), the last configuration the optimized SSC Φ_λ, which does not contribute to the energy after the MI-procedure.

The very small differences between the results before and after the MI show that it is sufficient in this case just to consider the wavefunction (13) as long as one is interested only in energies. The contribution of Φ_λ – equivalent to *all* the SSC's – is about 3‰ of the total correlation energy, an order of magnitude less than the errors arising from the deficiencies of our basis. And the recalculation of the higher NO's, i.e. the MI process itself, has almost no effect, it leads to an energy decrease of about 0.000003 a.u.

This behaviour is independent of the basis, it is merely the consequence of the smallness of the coefficients $d_{\alpha\alpha}$ for $\alpha > 1$, and cannot be expected if one of the $d_{\alpha\alpha}$ is comparable in its absolute value with d_1.

To study the influence of the SSC's on expectation values of one-electron operators we considered the operators x^2 (x being the molecular axis), y^2, r^2, $Q = 3x^2 - r^2$ (quadrupole moment of the electron charge distribution) and $F = r^{-5}(3x^2 - r^2)$ (field gradient of the electron charge distribution, calculated at the position of the nuclei). We can compare our results for E, $\langle x^2 \rangle$, $\langle y^2 \rangle$, $\langle Q \rangle$ with the very accurate results of Kolos and Wolniewicz [27]; comparison with experimental data is less valuable because the molecular vibrations are neglected in our calculations. Also for $\langle F \rangle$ Kolos-Roothaan-type calculations have been done [35], but the result seems not to be accessible to our knowledge. Very accurate calculations of $\langle F \rangle$ are necessary to determine the nuclear quadrupole moment of deuterium by nuclear quadrupole resonance [36].

The first thing we noticed was that our results depend significantly on the number of DSC's in the wavefunction. So we have tabulated in Table 2 the expectation values of the above operators calculated with MI-functions of the increasing size (1–14 determinants, 3 macroiterations) to test their convergency properties. The largest relative differences and the relative differences in the last step (from 9–14 determinants) are also given together with the results of Kolos and Wolniewicz [27]. Table 2 shows that all quantities seem to converge to the corresponding Kolos-Wolniewicz-values in more or less the same way as the energy itself, despite of the fact that only E varies monotonously.

Table 2. Macroiterated CI wavefunctions for H_2 ($R = 1.4 a_0$) with different numbers of configurations. Convergency test for the energy and some one-electron operators

Number of configurations	E (a.u.)	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle r^2 \rangle$	$\langle Q \rangle$	$\langle F \rangle$
1 (SCF)	−1.133095	2.0507	1.5508	5.1522	0.9999	0.3782
2	−1.151543	2.0621	1.5112	5.0844	1.1019	0.3799
3	−1.158925	2.0823	1.5347	5.1516	1.0953	0.3865
5	−1.169147	2.0624	1.5325	5.1274	1.0597	0.3793
9	−1.170885	2.0591	1.5284	5.1159	1.0615	0.3799
14	−1.171973	2.0554	1.5262	5.1079	1.0585	0.3802
Maximum relative differences (in ‰)	34	15	26	13	91	22
Relative differences in the last step (in ‰)	1	2	1	1	3	1
Values of Kolos and Wolniewicz [27]	−1.174470	2.0459	1.5234	5.0927	1.0451	

Table 3. Expectation values of some one-electron operators, calculated with the different wavefunctions. In parentheses: Differences with respect to the SCF-expectation value

Wavefunction	E (a.u.)	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle r^2 \rangle$	$\langle Q \rangle$	$\langle F \rangle$
(1) SCF-determinant	−1.133095	2.0507	1.5508	5.1522	0.9999	0.3782
(2) SCF-determinant + 13 DSC's	−1.171858	2.0667 (+0.0160)	1.5521 (+0.0013)	5.1710 (+0.0188)	1.0291 (+0.0292)	0.3752 (−0.0030)
(3) SCF-determinant + Brueckner term		2.0391 (−0.0116)	1.5253 (−0.0255)	5.0897 (−0.0625)	1.0277 (+0.0278)	0.3834 (+0.0052)
(4) SCF-determinant + 13 DSC's + Brueckner term	−1.171970	2.0562 (+0.0055)	1.5278 (−0.0230)	5.1118 (−0.0404)	1.0569 (+0.0570)	0.3801 (+0.0019)
(5) Contributions of (2) and (3) added to (1)		2.0551 (+0.0044)	1.5266 (−0.0242)	5.1085 (−0.0437)	1.0569 (+0.0570)	0.3804 (+0.0022)
(6) 14 determinant function after macroiteration	−1.171973	2.0554 (+0.0047)	1.5262 (−0.0246)	5.1079 (−0.0443)	1.0585 (+0.0586)	0.3802 (+0.0020)

Table 3 contains the expectation values of the same operators as above, in different stages of perfection to show the relative order of magnitude of the different contributions. The wavefunctions are

(1) SCF-determinant,
(2) SCF-determinant and DSC's,
(3) SCF-determinant and optimized SSC Φ_λ (Brueckner correction),
(4) wavefunction of Table 1 without MI, i.e. CI with SCF-determinant, DSC's and Φ_λ,
(5) contributions of (2) and (3) simply added to the SCF-result,
(6) full MI-wavefunction of Table 1.

The results of Table 3 show that the MI-treatment does not improve the values of (4) considerably – the same holds for the energy –, and further that the changes caused by admixing the DSC's and the Brueckner correction are to a good degree additive.

To answer the question whether the SCF- or the Brueckner-determinant yields better expectation values of one-electron operators we have to distinguish two cases:

(a) The contributions of the DSC's and of the Brueckner correction Φ_λ to the expectation value have more or less the same magnitude, but different signs (or they are both small). In this case the two corrections add up to about zero and the SCF-determinant gives already a good result. Examples in Table 3: $\langle x^2 \rangle, \langle F \rangle$.

(b) The two corrections have the same sign or they have different signs and rather different magnitude. Here the SCF-function is no longer a good approximation for calculating expectation values. Examples: $\langle y^2 \rangle, \langle r^2 \rangle, \langle Q \rangle$.

As can also be seen in Table 3 generally neither the correction due to the DSC's nor the Brueckner correction can be neglected; they contribute both up to 3% to the expectation values. Since different operators can behave differently and one does not know signs and magnitudes of the corrections in advance, one has to calculate (or to estimate) both to ensure that the SCF-values are good not only by chance.

In agreement with Larsson [18] we can conclude by stating that generally the Brueckner-determinant yields more accurate expectation values of one-electron operators than the SCF-determinant. This can be hidden if the corrections due to the DSC's and to Φ_λ are accidentally of the same magnitude and of different sign, but such a behaviour cannot be expected in advance.

4. The H_2 Molecule at Large Internuclear Separations

It is well known that the SCF-method fails to describe the behaviour of the H_2 potential energy curve at large internuclear distances, since the system of two H-atoms changes from a closed-shell state at equilibrium distance $R = R_0 = 1.4\,a_0$ to an open-shell one for $R \to \infty$. For $R = R_0$ the one-determinantal SCF-wavefunction $\Phi_1 = |1\sigma_g \overline{1\sigma_g}|$ is a good approximation of the exact wavefunction Ψ and a good starting point for the CI. For $R \to \infty$ this configuration becomes degenerate with $\Phi_2 = |1\sigma_u \overline{1\sigma_u}|$, therefore a wavefunction containing at least these two determinants is necessary to get the correct behaviour of the potential energy curve for large distances.

Since the coefficient of Φ_2 changes from about -0.1 at R_0 (see Sect. 3) to $-1/\sqrt{2}$ at $R \rightarrow \infty$, its influence backwards on Φ_1 increases and it becomes more and more necessary to change from the SCF-orbital to the first NO. This behaviour is typical for non-dynamical or degeneracy-type correlation [13]; other examples are Li_2 at large internuclear separations [20, 23] or CH_2 in its lowest $^1A_1$ state for nearly linear geometry [37, 38].

With our MI-treatment it is very easy to account for this behaviour. From the numerical point of view the situation for large distances becomes even more favourable than for small ones (see Sect. 3), because all higher NO's – except for $1\sigma_g$ and $1\sigma_u$ – become more and more unimportant, so we can go through all the MI-block with only the two configurations Φ_1 and Φ_2. These two contain only σ-type orbitals, so we can limit our basis for the MI-part of the calculation to σ-type basis functions.

We calculated the potential energy curve for H_2 in the range from $R = 1.4\,a_0$ to $R = 10.0\,a_0$ with a Gaussian basis set containing for each atom a 6s-Huzinaga basis [39] (contracted to 4 groups) augmented by three p-groups (exponents 1., 0.28, 0.08) in all three directions. The p_σ-group with the exponent 0.28 was uncoupled, so that our complete basis consisted of 48 Gaussian lobe functions contracted to 16σ, $6\pi_y$ and $6\pi_z$ groups. For $R = R_0$ this basis is poorer than the one used in Sect. 3, for large R it becomes rather good, the energy of two independent H-atoms calculated with this basis is -0.999881 a.u. [39].

Before we present the whole potential energy curve we pick out two of its points to show how differently the MI-procedure works in the two limiting cases where

a) $c_1 \approx 1$, all $|c_\alpha|$, $\alpha > 1$, very small, i.e. for $R \approx R_0$,

b) $|c_1| \approx |c_2| \approx 1/\sqrt{2}$, all $|c_\alpha|$, $\alpha > 2$, very small, i.e. for large R.

We have chosen the points $R = R_0 = 1.4a_0$ and $R = 5.0a_0$ and summarize some results in Table 4. In both calculations only the $|1\sigma_u \overline{1\sigma_u}|$ configuration is

Table 4. MI-procedure for H_2 at $R = 1.4\,a_0$ and $R = 5.0\,a_0$

		$R = 1.4$	$R = 5.0$
Without MI	$E_1 = E_{SCF}$	-1.133135	-0.859051
	E_2	-1.151390	-0.987635
	E_{13}	-1.170842	-0.988826
First MI	ΔE_λ	-0.000282	-0.013534
	c_λ	0.015337	0.146339
	E_1	-1.132842	-0.847547
	E_2	-1.151667	-1.001515
	Number of MI	2	5
Last MI	E_1	-1.132851	-0.836534
	E_2	-1.151667	-1.002728
After MI	E_{13}	-1.170950	-1.003387
	c_1	0.990987	0.793303
	c_2	-0.100458	-0.608349

All energies in a.u.

included in the MI-treatment which is completely sufficient for $R=5.0 a_0$, but leads to a small error for $R=R_0$, as will be shown later.

Because of this simplification of the MI-treatment the results for $R=R_0$ do not agree completely with those of our former calculation (Sect. 3). ΔE_λ, c_λ, the increase in E_1 and decrease in E_2 are much larger in Table 4 than in Table 1. But all these quantities are very small, the gain in the total energy E_{13} after MI is about 0.0001 a.u. in both calculations and can be neglected in comparison with the still remaining error of 0.0035 a.u. For $R=5.0 a_0$ the situation is completely different: ΔE_λ and c_λ are large, the decrease in E_2 and E_{13} cannot be neglected. Most of the energy is gained in the first MI, to reach self-consistency to six figures in the energy five macroiterations are necessary. But because the full basis – including the π-orbitals – is needed only for E_{13} and not in the SCF- and MI-steps, the computer time necessary for the MI-step is quite small. (For our basis we needed 10 sec for the evaluation of the integrals, 6 sec for the SCF-calculation, 3 sec for each MI, and 35 sec for the final determination of the higher NO's and the CI to calculate E_{13}, all for an IBM 360/85.)

Table 5 contains our results for the potential energy curve of H_2. For nine values of R from $R=R_0$ to $R=10.0 a_0$ we have tabulated the energies E_1, E_2, and E_{13}, calculated in three steps of increasing accuracy, namely:

a) standard CI with doubly substituted NO-configurations, using the approximation $\chi_1=\varphi_1$ (first NO = SCF-orbital), i.e. without MI-step;

b) after determination of the first NO χ_1, i.e. after MI-step, only one DSC is incorporated in the MI-block;

c) after determination of χ_1, but the four most important DSC's incorporated in the MI-block.

To enable comparison we have included in Table 5 the results of the "double configuration SCF" (DCSCF) calculation of Bowman, Hirschfelder, and Wahl [21] which must be compared with our E_2 of calculation b), and the nearly exact potential energy curve of Kolos and Wolniewicz [27].

Comparing these different calculations we come to the following conclusions:

1. Neither E_{SCF} nor E_{13} of calculation a) approaches the correct limit of two separate H atoms in their ground states (in our basis -0.999881 a.u.) for $R \to \infty$. Thus, the incorrect asymptotic behaviour of the SCF-energy is not fully balanced by the CI with only DSC's and the approximation $\chi_1=\varphi_1$.

2. After the determination of the first NO (MI-block in b) and c)) the correct behaviour of E_2 and E_{13} for large R is obtained. For $R \to \infty$ the difference between our calculations and those of Kolos and Wolniewicz [27] or Bowman, Hirschfelder and Wahl [21] are only due to the deficiency of our Gaussian basis. For small R our results are poorer, because we did not optimize our basis to give a good description of the bonding region.

3. For large R the difference between E_{13} and E_2 should be equal to the London dispersion energy [40]. Its leading term is $-6.5 R^{-6}$ a.u. [41, 42], while we got -0.000007 a.u. for $R=10.0 a_0$.

4. The differences in E_2 and E_{13} between the two calculations b) and c) are rather small, but noticeable for $R=R_0$, they become smaller for increasing R, and are less than 0.000001 a.u. for $R \geqq 6.0 a_0$. (Therefore we did not perform the much more time consuming calculation c) for $R \geqq 6.0 a_0$.) That is due to the fact that the

Table 5. Potential energy curve of H_2 (all energy values are negative)

R	$1.4\,a_0$	$1.6\,a_0$	$2.0\,a_0$	$3.0\,a_0$	$4.0\,a_0$	$5.0\,a_0$	$6.0\,a_0$	$8.0\,a_0$	$10.0\,a_0$
a) E_{SCF}	1.133135	1.126001	1.091374	0.989186	0.911505	0.859051	0.824326	0.785618	0.766951
E_2	1.151390	1.147266	1.119834	1.044436	1.003452	0.987635	0.982312	0.980752	0.981815
E_{13}	1.170842	1.165126	1.134139	1.052096	1.006544	0.988826	0.982899	0.981038	0.982018
b) E_1	1.132851	1.125578	1.090491	0.984823	0.898614	0.836534	0.795992	0.755630	0.738548
E_2	1.151667	1.147675	1.120677	1.048180	1.013025	1.002728	1.000437	0.999899	0.999882
E_{13}	1.170950	1.165329	1.134714	1.055243	1.015417	1.003387	1.000622	0.999927	0.999889
c) E_1	1.133030	1.125808	1.090878	0.985669	0.899773	0.837399			
E_2	1.151621	1.147629	1.120618	1.048139	1.013004	1.002721			
E_{13}	1.170975	1.165354	1.134724	1.055264	1.015429	1.003390			
E(DCSCF)	1.152148	1.147992	1.120896	1.048092	1.013088	1.002847	1.000555	1.000018	1.000000_5
$E(K-W)$	1.174474	1.168580	1.138131	1.057312	1.016369	1.003763	1.000815	1.000053	1.000009_1

a), b), c) description see text, all energies in a.u.

coefficients c_3, c_4, c_5 of the configurations Φ_3, Φ_4, and Φ_5 – being about -0.05 at $R = R_0$ (compare Table 1) – decrease very rapidly with increasing R, whereas c_2 increases from about -0.1 at $R = R_0$ to $-1/\sqrt{2}$ for $R \to \infty$.

Thus, we can conclude by stating that our MI-treatment to determine the first NO enables us to get rather good results even in unfavourable cases, when the CI-coefficients of one or more excited configurations are large. Especially, the behaviour of potential energy curves can be obtained correctly. This is of special importance for the interaction of atoms or molecules at large internuclear distances.

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