

PERTURBATION THEORY OF INTERMOLECULAR FORCES IN THE SMALL OVERLAP REGION. PART II*

L. PIELA AND B. JEZIORSKI

Institute of Basic Problems of Chemistry, University of Warsaw**

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Three new perturbation procedures for the calculation of the exchange forces between atoms or molecules are proposed and tested in the case of the ground and the first excited states of the hydrogen molecule. All these procedures have the Rayleigh-Schrödinger framework and are based on the method which has been described in a previous paper [1]. For comparison, numerical calculations have also been performed by using the Hirschfelder-Silbey (HS), Murrell-Shaw-Musher-Amos (MS-MA) and Hirschfelder-van der Avoird (HAV) procedures. All interaction energies through the second order, with the exception of the HAV result, are similar and coincide very well with the variational energy obtained with the same basis set. Some of the new formalisms give a much better Coulomb energy than the methods used until now.

1. Introduction

In Part I a Rayleigh-Schrödinger type perturbation method has been developed (hereafter called method I) for calculation of the interaction energies between molecules in the region of small overlap [1]. The method takes into account the symmetry requirements for the unperturbed wave function, which has been taken as

$$\psi_0 = N_0 A \varphi_0, \quad (1)$$

where the operator A projects on the space of functions having symmetry properties of the state under consideration and N_0 is a normalization constant. The φ_0 function can be any arbitrary function subject to some general requirements specified in Part I. In particular, φ_0 can be chosen as a simple product of the exact wave functions of both interacting molecules.

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** Address: Instytut Podstawowych Problemów Chemii, Uniwersytet Warszawski, Warszawa, Pasteura 1, Poland.

Using two projectors

$$Q = |\psi_0\rangle\langle\psi_0| \quad (2)$$

and

$$S = A - Q \quad (3)$$

the total Hamiltonian H or more exactly its part in $A\mathfrak{S}$ space (\mathfrak{S} denotes the total Hilbert space) has been divided into four parts

$$AH = QHQ + SHS + SHQ + QHS. \quad (4)$$

The operators SHQ and QHS vanish at infinite intermolecular distance R and can be included into the perturbation. In order to assure the Rayleigh-Schrödinger framework of the theory, it has been necessary to split the SHS term into two hermitean parts: the "small" one vanishing for $R \rightarrow \infty$ and the "large" one remaining finite at infinite intermolecular separation. This has been done by using the operator T [1]:

$$T = \sum_{k=1}^{\infty} |\Phi_k\rangle\langle\Psi_k|, \quad (5)$$

where Ψ_k form an orthonormal basis in the $S\mathfrak{S}$ space and functions Φ_k , defined exactly in [1], satisfy the relation

$$\Psi_k = A\Phi_k. \quad (6)$$

In order to understand more deeply the characteristic features of the theory of exchange interactions let us turn to group theory.

If one introduces group algebras [2] AG , AG_0 and AG_1 corresponding to G , G_0 and $G_1 = G \cap G_0$ groups, respectively; the symmetry properties of the operators H and H_0 can be included in the following commutation relations:

$$\begin{aligned} [g, H_0] &= 0 & \text{for } g \in AG_0 \\ [g, H] &= 0 & \text{for } g \in AG \\ [g, H_0] &\neq 0 & \text{for } g \in AG \text{ and } g \notin AG_1. \end{aligned} \quad (7)$$

Since the operators H , H_0 and $V = H - H_0$ contain the co-ordinates of the nuclei of both molecules, they depend parametrically on $\lambda = 1/R$ and one can write

$$H(\lambda) = H_0(\lambda) + V(\lambda). \quad (8)$$

Using the explicit form of $V(\lambda)$ one can easily show that this operator is "small" on all finite-dimensional stable subspaces of the operator $H_0(\lambda)$, i.e.

$$\lim_{\lambda \rightarrow 0} V(\lambda)\varphi(\lambda) = 0, \quad (9)$$

where $\varphi(\lambda)$ is the finite sum of eigenvectors of $H_0(\lambda)$. Generally, however, commutation relations (7) make fulfilment of equation (9) impossible in the whole Hilbert space \mathfrak{S} .

Actually, if g_1 and g_2 does not belong to AG_0 and if $\varphi_k(\lambda)$ are eigenvectors of $H_0(\lambda)$ then:

$$\begin{aligned} \lim_{\lambda \rightarrow 0} \langle g_1 \varphi_k(\lambda) | V(\lambda) | g_2 \varphi_l(\lambda) \rangle &= \lim_{\lambda \rightarrow 0} [\langle g_1 \varphi_k(\lambda) | g_2 V(\lambda) | \varphi_l(\lambda) \rangle + \\ + \langle g_1 \varphi_k(\lambda) | [g_2, H_0] | \varphi_l(\lambda) \rangle] &= \lim_{\lambda \rightarrow 0} \langle \varphi_k(\lambda) | g_1^\dagger [g_2, H_0] | \varphi_l(\lambda) \rangle \neq 0 \end{aligned} \quad (10)$$

because $[g_2, H_0] \neq 0$.

Therefore, since $V(\lambda) \cdot (\psi_{\text{exact}} - \varphi_0)$ must not be neglected in the derivation of the first order perturbational equation, the operator $V(\lambda)$ cannot be used as a perturbation in the usual perturbational procedure. The perturbation operator \mathcal{V} of Part I (as well as those \mathcal{V} , which will be introduced below) is small in a much stronger sense than $V(\lambda)$, namely

$$\lim_{\lambda \rightarrow 0} \mathcal{V}(\lambda) g \varphi_k = 0 \quad (11)$$

for any arbitrary element g of the group algebra AG .

2. Intramolecular and intermolecular symmetry operations

Let us consider two molecules a and b with n and m electrons respectively and with fixed configurations of nuclei within each molecule. Let the molecules be shifted along an axis without rotations and without changes of intramolecular geometry. Thus, the configuration of the nuclei can be uniquely determined by the intermolecular distance R , which might be for instance the separation between arbitrarily chosen atoms of both molecules.

The total wave function ψ of the interacting molecules belongs to an irreducible representation of the symmetry group G of the system. This group is the direct product of the point group \mathcal{F} and the permutation group \mathcal{S}_N of all $N = n + m$ electrons of both molecules *i. e.* $G = \mathcal{F} \otimes \mathcal{S}_N$

We assume that \mathcal{F} consists of only those operations F , which exist at all values of R . If there exist such F which exchange the nuclei of the molecule a with those of the molecule b , then the interaction will be called homomolecular otherwise heteromolecular. If additionally in a homomolecular case n equals m , then the interaction will be called isoelectronic.

The irreducible representation (corresponding to the state under consideration) of G is the direct product of a proper irreducible representation of \mathcal{F} characterized by the projector C and the irreducible representation of \mathcal{S}_N connected with the projector (antisymmetrizer) A

$$C = \frac{1}{|\mathcal{F}|} \sum_{F \in \mathcal{F}} \chi(F^{-1}) F \quad (12)$$

$$A = \frac{1}{N!} \sum_{P \in \mathcal{S}_N} (-1)^P P, \quad (13)$$

where l and $|\mathcal{F}|$ denote the dimension of the proper irreducible representation and the order of the group \mathcal{F} , respectively, χ denotes characters of this irreducible representation and P the permutation operations of electrons of both molecules.

The general projection operator A associated with a given irreducible representation of a whole symmetry group of the system can be written as a product

$$A = BCA, \quad (14)$$

where the additional projector B assures that, for an arbitrary Φ , $A\Phi$ is an eigenfunction of the square of the total spin. The operator B can be constructed, for instance, using the Löwdin projectors [3].

Let us take now the group $\mathcal{S}_0 = \mathcal{S}_n \otimes \mathcal{S}_m$, which consists of all permutations which do not exchange electrons between molecules. The set of all $P \in \mathcal{S}_N - \mathcal{S}_0$ will be denoted by \mathcal{S}_{ex} . In the case when both interacting molecules are isoelectronic, there exists a non-empty set $\mathcal{S}_{ab} \subset \mathcal{S}_{\text{ex}}$ of such P which exchange all electrons of the molecule a with all electrons of the molecule b .

The \mathcal{S}_{ab} set can be rigorously defined by

$$\mathcal{S}_{ab} = P_{ab}\mathcal{S}_0, \quad (15)$$

where

$$\mathcal{S}_{\text{ex}} \ni P_{ab} = (1, n+1)(2, n+2)\dots(n, 2n). \quad (16)$$

The antisymmetrizer can be separated into two parts

$$A = A_+ + A_-, \quad (17)$$

where

$$A_+ = \frac{1}{N!} \sum_{P \in \mathcal{S}_0} (-1)^P P \quad (18)$$

$$A_- = \frac{1}{N!} \sum_{P \in \mathcal{S}_{\text{ex}}} (-1)^P P. \quad (19)$$

One can easily see that if A_a and A_b denote the antisymmetrizers of electrons $1 \dots n$ and $n+1, \dots, n+m$, respectively, then

$$A_+ = \frac{n!m!}{N!} A_a A_b. \quad (20)$$

Let us denote by \mathcal{F}_0 the subgroup of \mathcal{F} , which includes those $F \in \mathcal{F}$, which do not exchange any atoms between molecules. Let the set $\mathcal{F} - \mathcal{F}_0$ be denoted by \mathcal{F}_{ex} . If \mathcal{F}_{ex} is not an empty set, then the interaction is homomolecular otherwise it is heteromolecular. Now, it is possible to write

$$C = C_+ + C_-, \quad (21)$$

where

$$C_+ = \frac{l}{|\mathcal{F}|} \sum_{F \in \mathcal{F}_0} \chi(F^{-1})F \quad (22)$$

and

$$C_- = \frac{l}{|\mathcal{F}|} \sum_{F \in \mathcal{F}_{\text{ex}}} \chi(F^{-1})F. \quad (23)$$

The projector A of Equation (14) can be written as

$$A = BCA = \mathbf{B} \frac{l}{N!|\mathcal{F}|} \sum_{P \in \mathcal{S}_N} (-1)^P P \sum_{F \in \mathcal{F}} \chi(F^{-1})F = A_+ + A_- \quad (24)$$

where

$$A_+ = \frac{l}{N!|\mathcal{F}|} \mathbf{B} \sum_{PF \in G_1} (-1)^P \chi(F^{-1})PF, \quad (25)$$

$$A_- = \frac{l}{N!|\mathcal{F}|} \mathbf{B} \sum_{G \ni PF \approx G_1} (-1)^P \chi(F^{-1})PF. \quad (26)$$

Since G_1 is the subgroup of G_0 and G , then from Equation (25) it follows that $A_+^\dagger = A_+$.

Let us investigate A_+ in greater detail

$$\begin{aligned} A_+ &= \frac{l}{N!|\mathcal{F}|} \mathbf{B} \left[\sum_{P \in \mathcal{S}_0} \sum_{F \in \mathcal{F}_0} (-1)^P \chi(F^{-1})PF + \right. \\ &+ \left. \sum_{P \in \mathcal{S}_{ab}} \sum_{F \in \mathcal{F}_{\text{ex}}} (-1)^P \chi(F^{-1})PF \right] = \mathbf{B}(C_+A_+ + C_-A_{ab}) \end{aligned} \quad (27)$$

where

$$A_{ab} = \frac{1}{N!} \sum_{P \in \mathcal{S}_{ab}} (-1)^P P = (-1)^n P_{ab} A_+. \quad (28)$$

Since in the non-isoelectronic homomolecular interaction \mathcal{S}_{ab} is an empty set and in the heteromolecular interaction \mathcal{F}_{ex} is an empty set, then

$$A_+ = \begin{cases} \mathbf{B}(C_+A_+ + C_-A_{ab}) = \mathbf{B} \frac{(n!)^2}{N!} (C_+ + (-1)^n C_- P_{ab}) A_+ A_b \\ \mathbf{B} C_+ A_+ \\ \mathbf{B} C A_+ \end{cases} \quad (29)$$

$$A_- = \begin{cases} \mathbf{B}[C_-A_+(1 + (-1)^{n+1} P_{ab}) + C A_-] \\ \mathbf{B}(C_-A_+ + C A_-) \\ \mathbf{B} C A_- \end{cases} \quad (30)$$

The first row of Equations (29) and (30) refers to homomolecular isoelectronic interactions, the second one — to homomolecular non-isoelectronic interactions and the third one — to heteromolecular interactions.

The operators A_+ and A_- will be used in the next section for the construction of perturbational procedures of the Rayleigh-Schrödinger type.

3. Method II

The splitting of the SHS term of Equation (4) performed in Part I is by no means the only one possible. Using Equation (24) one can divide SHS into three parts

$$SHS = T^{\dagger}H_0A_+T + T^{\dagger}VA_+T + T^{\dagger}HA_-T \quad (31)$$

The Equation (31) can be easily verified by means of the relations $AT = S$, $S^{\dagger} = S$ and Equation (8).

Now, AH in the Schrödinger equation

$$AH\psi = E\psi \quad (32)$$

can be separated into

$$AH = \mathcal{H}_0 + \mathcal{V}, \quad (33)$$

where

$$\mathcal{H}_0 = E_0Q + T^{\dagger}H_0A_+T \quad (34)$$

$$\mathcal{V} = \Delta E_{HL}Q + SHQ + QHS + T^{\dagger}VA_+T + T^{\dagger}HA_-T \quad (35)$$

and

$$\Delta E_{HL} = \langle \psi_0 | H - E_0 | \psi_0 \rangle. \quad (36)$$

Note that since $TQ = 0$ (see [1]), ψ_0 is an eigenfunction of \mathcal{H}_0

$$\mathcal{H}_0\psi_0 = E_0\psi_0. \quad (37)$$

If the Heitler-London function is chosen as ψ_0 , then ΔE_{HL} is the Heitler-London correction to the energy. The \mathcal{H}_0 unperturbed operator is self-adjoint since $H_0A_+ = A_+H_0$ and $A_+^{\dagger} = A_+$. Since additionally \mathcal{H}_0 commutes with A , one can use the familiar Rayleigh-Schrödinger perturbation theory. The first order correction to the energy $E^{(1)}$ equals ΔE_{HL} , because $\psi_0 = Q\psi_0$ and $QS = TQ = 0$. Note that the perturbation at sufficiently large distances R is certainly small, because QHS and SHQ operators are small [1] and all matrix elements of the $T^{\dagger}VA_+T$ and $T^{\dagger}HA_-T$ operators vanish for $R \rightarrow \infty$.

To calculate the first order correction to the wave function, $\psi^{(1)}$, the following functional should be minimized

$$\begin{aligned} \tilde{E}^{(2)} = & \langle T\tilde{\psi}^{(1)} | H_0A_+ - E_0S | T\tilde{\psi}^{(1)} \rangle + \\ & + N_0 \langle \tilde{\psi}^{(1)} | V | \varphi_0 \rangle + N_0 \langle \varphi_0 | V | \tilde{\psi}^{(1)} \rangle, \end{aligned} \quad (38)$$

where the trial function $\tilde{\psi}^{(1)} \in \mathcal{S}\mathcal{S}$.

To minimize the expression (38) one can expand $\tilde{\psi}^{(1)}$ in a finite series of M functions Ψ_k and use the Ritz variational method. Owing to the A_+ operator, the calculations through the second order need a very small number of multicenter integrals (with centers belonging to both molecules). The number of exchange integrals which are the most time consuming is proportional to M since they appear in the last two terms of Equation (38). This may be compared with the numerical effort of variational calculations with the number of exchange integrals proportional to M^2 .

The second order energy can be evaluated from

$$E^{(2)} = \langle \psi^{(1)} | \mathcal{V} | \psi_0 \rangle = N_0 \langle \psi^{(1)} | V | \varphi_0 \rangle. \quad (39)$$

The present method is very similar to the matrix perturbational method of Pecul [4]. However, the matrix elements of the \mathcal{H}_0 operator and the elements of the U matrix in Pecul's method differ slightly, because Pecul used asymptotic values of normalization constants in the basis functions Ψ_k . As his zeroth order energy Pecul used $E_0 + \Delta E_{HL}$. This difference is not an essential one, because the $\Delta E_{HL} Q$ term can be included in \mathcal{V} as well as in \mathcal{H}_0 . The last statement is also true for the method I as well as for two other methods developed below.

4. Method III

Let us investigate more thoroughly the operator \mathcal{V} . The QHS and SHQ terms in \mathcal{V} assure that ψ_0 is an eigenfunction of the \mathcal{H}_0 operator. If one calculates the energy using the method II through the second order, then the last two terms in \mathcal{V}_{0k} vanish since $TQ = QT = 0$.

Nevertheless, these terms do affect indirectly the second order energy, since they determine \mathcal{H}_0 through Equation (33). If the last two terms in \mathcal{V} were included into \mathcal{H}_0 , then the second order calculation would require all the same integrals as the variational method and therefore would be impractical.

However, most of the time-consuming intermolecular exchange integrals are generated by the $T^\dagger HA_- T$ term. These integrals vanish exponentially as R tends to infinity in contrast to the integrals generated by the $T^\dagger VA_+ T$ term, which as a rule behave like R^{-k} .

Thus, one can see that for sufficiently large distances the $T^\dagger HA_- T$ operator should be smaller than $T^\dagger VA_+ T$. If one shifts the $T^\dagger VA_+ T$ term to \mathcal{H}_0 , then one can expect the perturbation to become significantly smaller and the perturbation series to converge, faster. So, one obtains

$$\mathcal{H}_0 = E_0 Q + T^\dagger HA_+ T \quad (40)$$

$$\mathcal{V} = \Delta E_{HL} Q + SHQ + QHS + T^\dagger HA_- T. \quad (41)$$

It can be easily seen, that similarly as in the case of the method II, the operator \mathcal{H}_0 satisfies the relations

$$\mathcal{H}_0^\dagger = \mathcal{H}_0 \quad (42)$$

$$[\mathcal{H}_0, A] = 0 \quad (43)$$

$$\mathcal{H}_0 \psi_0 = E_0 \psi_0. \quad (44)$$

The operators \mathcal{H}_0 and \mathcal{V} obtained in the above way can be used in the Rayleigh-Schrödinger perturbation procedure as the unperturbed operator and the perturbation respectively. The functional to be minimized in the second order calculation could be obtained by replacing \mathcal{H}_0 by H in Equation (38).

The method III is numerically more complicated than the method I and II, because of a great number of Coulomb integrals, which should be evaluated. However, one can expect, that especially for larger distances this method should give better second order energy than other methods do.

5. Method IV

The last term of Equation (41) can be separated in the following way

$$T^\dagger H A_- T = \frac{1}{2} T^\dagger [(H - U_{ab})A_- + A_-(H - U_{ab})]T + \frac{1}{2} T^\dagger (U_{ab}A_- + A_-U_{ab})T, \quad (45)$$

where

$$U_{ab} = \sum_{i=1}^n \sum_{j=n+1}^{n+m} \frac{1}{r_{ij}}. \quad (46)$$

Now, shifting to \mathcal{H}_0 the first term of the right-hand side of Equation (45) one obtains a new partition of the AH operator:

$$\mathcal{H}_0 = E_0 Q + T^\dagger H A_+ T + \frac{1}{2} T^\dagger [(H - U_{ab})A_- + A_-(H - U_{ab})]T \quad (47)$$

$$\mathcal{V} = \Delta E_{\text{HL}} Q + S H Q + Q H S + \frac{1}{2} T^\dagger (U_{ab}A_- + A_-U_{ab})T. \quad (48)$$

One can easily see that Equations (42)–(44) remain true. The new \mathcal{H}_0 and \mathcal{V} operators can be used in the usual way to construct the perturbational scheme. The first order correction to the wave function should minimize the following functional

$$\begin{aligned} \bar{E}^{(2)} = & \langle T \tilde{\psi}^{(1)} | H A - \frac{1}{2} (U_{ab}A_- + A_-U_{ab}) - E_0 S | T \tilde{\psi}^{(1)} \rangle + \\ & + N_0 \langle \tilde{\psi}^{(1)} | V | \varphi_0 \rangle + N_0 \langle \varphi_0 | V | \tilde{\psi}^{(1)} \rangle. \end{aligned} \quad (49)$$

Due to the fact, that the $\frac{1}{2} T^\dagger (U_{ab}A_- + A_-U_{ab})T$ term is included in the perturbation \mathcal{V} , the calculations of $E^{(2)}$ need only a small part (the same as in the previously described methods) of the intermolecular exchange integrals appearing in the variational method.

6. Numerical example

One may ask the following questions: (i) which one of the new formalisms gives the best interaction (E_{int}), exchange (E_{exch}) and Coulomb (E_{Coul}) energies through the second order, (ii) are the above quantities better or not than those predicted by methods used until now. The authors try to give a partial answer to these questions by calculating $\bar{E}^{(2)}$,

E_{exch} and \bar{E}_{Coul} for the two lowest states ($X^1\Sigma_g^+$ and $b^3\Sigma_u^+$) of the hydrogen molecule using a limited basis set in the $S\mathfrak{S}$ space (hereafter all quantities calculated using a finite basis set will be indicated by a bar).

The hydrogen molecule has been chosen to assure relative simplicity of calculations and also because in this case numerous accurate calculations have been performed by the variational as well as perturbational methods.

In the present paper the authors use the methods:

I — developed in Part I.

II, III, IV — described in the present paper.

HS — the method given by Hirschfelder and Silbey [5].

HAV — the method of Hirschfelder and van der Avoird [6].

MS-MA — the method given by Múschler, Amos, Murrell and Shaw [7].

The present authors have used also another version of the methods I–IV with the zeroth order energy equal to $E_0 + \Delta E_{\text{HL}}$ instead of E_0 . This can be done by shifting the $\Delta E_{\text{HL}}Q$ term from \mathcal{V} to \mathcal{H}_0 in each of our methods. For $R = 8$ a. u. the results of this alternative version differ only slightly from the corresponding ones of the original versions; for larger R both sets of results are identical.

Recently Pecul [4] has carried out perturbational calculations for the hydrogen molecule using his own method (hereafter denoted by P) as well as the variational approach with the same basis set for $R = 8, 10$ and 12 a. u. Since the comparison of the perturbational results with the best possible ones in the same basis set (variational) is of special interest, we decided to carry out our perturbational calculations for the same intermolecular distances and the same basis sets.

The $\psi^{(1)}$ in the $S\mathfrak{S}$ space has been expanded in terms of the Ψ_k functions of Equation (6). The Ψ_k functions have been constructed as in Part I from the Slater type orbitals (with all orbital exponents equal 1). For $R = 8$ and 10 a. u. the eleven term expansion has been used consisting of configurations: $2p\ 2p, 2p\ 3p, 2p\ 3d, 2p\ 4f, 3d\ 3d$ and for $R = 12$ a. u. the nine term expansion with the same configurations but with only $3d_0\ 3d_0$ function from the $3d\ 3d$ type configurations.

In Tables I and II the second order corrections to the energy ($\bar{E}^{(2)}$) are given for the ground and the first excited states respectively together with $\bar{E}_{\text{var}} - (E_0 + \Delta E_{\text{HL}})$. The symbol \bar{E}_{var} denotes the variational energy calculated with the same basis set as the perturbational quantities. The ΔE_{HL} values and values defined by

$$\bar{\Delta} = \frac{(E_0 + \Delta E_{\text{HL}} + \bar{E}^{(2)}) - \bar{E}_{\text{var}}}{\bar{E}_{\text{var}} - E_0 - \Delta E_{\text{HL}}} \quad (50)$$

are also given.

It can be easily proved using the matrix formulation of the perturbational method, that for the Rayleigh-Schrödinger perturbational procedures

$$\bar{\Delta} \cong - \frac{\bar{E}^{(3)} + \bar{E}^{(4)} + \dots}{\bar{E}^{(2)}} \quad (51)$$

TABLE I

Comparison of the second order corrections to the energy ($\bar{E}_s^{(2)}$) with $\bar{E}_{\text{var}}^s - (E_0 + \Delta E_{\text{HL}}^s)$ for the ground state ($X^1\Sigma_g^+$) of the hydrogen molecule. In the last row the Heitler-London corrections to the energy ΔE_{HL}^s are listed. Energies in cm^{-1} , R in a.u., $\bar{A}_s = [(E_0 + \Delta E_{\text{HL}}^s + \bar{E}_s^{(2)}) - \bar{E}_{\text{var}}^s] \cdot (\bar{E}_{\text{var}}^s - E_0 - \Delta E_{\text{HL}}^s)^{-1}$

Method \ R	$\bar{E}_s^{(2)}$			\bar{A}_s in percent		
	8	10	12	8	10	12
I	-7.423	-1.742	-0.5433	+1.4	+0.13	-0.066
II	-7.304	-1.735	-0.5430	-0.23	-0.26	-0.12
P	-7.306	-1.736	-0.5430	-0.21	-0.24	-0.10
III	-7.239	-1.734	-0.5434	-1.1	-0.33	-0.042
IV	-7.516	-1.746	-0.5438	+2.7	+0.36	+0.031
HS	-7.472	-1.743	-0.5432	+2.1	+0.15	-0.072
MS-MA	-7.471	-1.743	-0.5432	+2.1	+0.15	-0.072
HAV	-3.873	-0.876	-0.2718	-47.1	-49.6	-50.0
variational	-7.321	-1.740	-0.5436	—	—	—
ΔE_{HL}^s	-3.817	$-1.130 \cdot 10^{-1}$	$-3.051 \cdot 10^{-3}$	—	—	—

TABLE II

Comparison of the second order corrections to the energy ($\bar{E}_t^{(2)}$) compared with $\bar{E}_{\text{var}}^t - (E_0 + \Delta E_{\text{HL}}^t)$ for the first excited state ($b^3\Sigma_u^+$) of the hydrogen molecule. In the last row the Heitler-London corrections to the energy ΔE_{HL}^t are listed. Energies in cm^{-1} , R in a.u., $\bar{A}_t = [(E_0 + \Delta E_{\text{HL}}^t + \bar{E}_t^{(2)}) - \bar{E}_{\text{var}}^t] \cdot (\bar{E}_{\text{var}}^t - E_0 - \Delta E_{\text{HL}}^t)^{-1}$

Method \ R	$\bar{E}_t^{(2)}$			\bar{A}_t in percent		
	8	10	12	8	10	12
I	-7.041	-1.724	-0.5426	+0.44	+0.019	-0.074
II	-7.180	-1.731	-0.5429	+2.4	+0.42	-0.027
P	-7.174	-1.731	-0.5429	+2.3	+0.40	-0.029
III	-7.110	-1.730	-0.5433	+1.4	+0.34	+0.043
Iv	-6.820	-1.718	-0.5429	-2.7	-0.36	-0.030
HS	-6.983	-1.724	-0.5427	-0.39	-0.007	-0.069
MS-MA	-6.983	-1.724	-0.5427	-0.39	-0.007	-0.069
HAV	-3.384	-0.857	-0.2712	-51.7	-50.3	-50.1
variational	-7.010	-1.724	-0.5430	—	—	—
ΔE_{HL}^t	+3.032	$+9.185 \cdot 10^{-2}$	$+2.516 \cdot 10^{-3}$	—	—	—

The exchange and Coulomb energies are defined by

$$\bar{E}_{\text{exch}} = \frac{1}{2} (\bar{E}_{\text{int}}^s - \bar{E}_{\text{int}}^t) \quad (52)$$

$$\bar{E}_{\text{Coul}} = \frac{1}{2} (\bar{E}_{\text{int}}^s + \bar{E}_{\text{int}}^t), \quad (53)$$

where

$$\bar{E}_{\text{int}}^v = \begin{cases} \Delta E_{\text{HL}}^v + \bar{E}_v^{(2)} & \text{for perturbational methods} \\ \bar{E}_{\text{var}}^v - E_0 & \text{for the variational method} \end{cases} \quad (54)$$

and $v = s$ or $v = t$ for the singlet and triplet states respectively.

The exchange and Coulomb energies are collected in Tables III and IV respectively. The relative deviations of the exchange and Coulomb energies calculated perturbationally (\bar{E}_{exch}^p and \bar{E}_{Coul}^p) from the variational ones ($\bar{E}_{\text{exch}}^{\text{var}}$ and $\bar{E}_{\text{Coul}}^{\text{var}}$) are denoted by $\bar{\Delta}_{\text{exch}}$ and $\bar{\Delta}_c$ respectively

$$\bar{\Delta}_{\text{exch}} = (\bar{E}_{\text{exch}}^p - \bar{E}_{\text{exch}}^{\text{var}}) / \bar{E}_{\text{exch}}^{\text{var}} \quad (55)$$

$$\bar{\Delta}_c = (\bar{E}_{\text{Coul}}^p - \bar{E}_{\text{Coul}}^{\text{var}}) / \bar{E}_{\text{Coul}}^{\text{var}} \quad (56)$$

They are also given in Tables III and IV.

7. Discussion

One can see from the Tables I-IV that the results of various perturbational methods are close to the variational values. The only exception is the HAV method, which gives very poor interaction and Coulomb energies. The values of $\bar{\Delta}_s$, $\bar{\Delta}_i$ and $\bar{\Delta}_c$ for this method tend to 50% as R increases. It agrees with the previous observations [8], that the second order corrections to the energy in the HAV method approach 50% of the dispersion energy.

It is very well known, that the HAV method is able to give good interaction energy, when the third order correction $E^{(3)}$ is taken into consideration [9]. However, in our opinion a perturbational method is of any practical value, only if it gives satisfactory results already in the second order calculations. Only in this case it requires much less computational effort than the usual variational method.

One can also see that for $R = 8, 10, 12$ a. u. the results of the HS method are very close to those of the MS-MA method and similarly the method P gives results close to those of the method II (although in the last case the discrepancies are greater). The coincidence of the HS and MS-MA results for $R = 8$ is known from the literature [8].

It follows from Tables I and II that no method gives the best interaction energies for all values of R and for both states under consideration. For $R = 8$ and 10 a. u. the best methods are: I, II, III for the singlet and HS, MS-MA and I for the triplet states.

One can expect that III and IV methods should be better than others at large intermolecular distances since the corresponding perturbation operators consists of fewer terms vanishing as R^{-k} . It has been found that for both states under consideration the method IV is relatively poor at $R = 8$ and 10 a. u. but it is the best one at $R = 12$ a. u. The method III is fairly good in comparison to other methods for $R = 8$ and 10 a. u. (for both states), but is very good for $R = 12$ a. u.

As one can see from the Table III, the method I gives the best exchange energy except at $R = 12$ a. u., where it gives a slightly worse result than the HS, HAV and MS-MA methods. All three last methods give the same values of the exchange energy for $R = 8, 10, 12$ a. u. The methods III and IV give the worst results of the exchange energy, even at $R = 12$ a. u., where these methods give the best interaction energy.

It appears from the Table IV that the methods III and IV give a definitely better Coulomb energy than any other method. The difference between these methods occurs only at $R = 8$ a. u., where the method IV is the best one. All other methods (except the HAV

TABLE III

The perturbational exchange energies compared to the variational ones*. Energies in cm^{-1} , R in a.u.,

$$\bar{\Delta}_{\text{exch}} = (\bar{E}_{\text{exch}}^p - \bar{E}_{\text{exch}}^{\text{var}}) / \bar{E}_{\text{exch}}^{\text{var}}$$

Method \ R	\bar{E}_{exch}			$\bar{\Delta}_{\text{exch}}$ in percent		
	8	10	12	8	10	12
I	-3.616	$-1.114 \cdot 10^{-1}$	$-3.11 \cdot 10^{-3}$	+0.98	+0.91	+0.65
II	-3.487	$-1.046 \cdot 10^{-1}$	$-2.86 \cdot 10^{-3}$	-2.6	-5.3	-8.1
P	-3.491	$-1.048 \cdot 10^{-1}$	$-2.87 \cdot 10^{-3}$	-2.5	-5.1	-8.4
III	-3.489	$-1.046 \cdot 10^{-1}$	$-2.86 \cdot 10^{-3}$	-2.5	-5.3	-8.1
IV	-3.773	$-1.167 \cdot 10^{-1}$	$-3.26 \cdot 10^{-3}$	+5.4	+5.7	+5.5
HS	-3.669	$-1.118 \cdot 10^{-1}$	$-3.08 \cdot 10^{-3}$	+2.5	+1.3	-0.32
MS-MA	-3.669	$-1.118 \cdot 10^{-1}$	$-3.08 \cdot 10^{-3}$	+2.5	+1.3	-0.32
HAV	-3.670	$-1.118 \cdot 10^{-1}$	$-3.08 \cdot 10^{-3}$	+2.5	+1.3	-0.32
variational	-3.581	$-1.104 \cdot 10^{-1}$	$-3.09 \cdot 10^{-3}$	—	—	—

* $\bar{E}_{\text{exch}}^{\text{var}}$ and \bar{E}_{exch}^p label respectively the exchange energies calculated variationally and perturbationally through the second order

TABLE IV

The perturbational Coulomb energies compared to the variational ones*. Energies in cm^{-1} , R in a.u.,

$$\bar{\Delta}_c = (\bar{E}_{\text{Coul}}^p - \bar{E}_{\text{Coul}}^{\text{var}}) / \bar{E}_{\text{Coul}}^{\text{var}}$$

Method \ R	\bar{E}_{Coul}			$\bar{\Delta}_c$ in percent		
	8	10	12	8	10	12
I	-7.6251	-1.7439	-0.54322	+0.88	+0.075	-0.070
II	-7.6352	-1.7440	-0.54322	+1.0	+0.080	-0.070
P	-7.6330	-1.7439	-0.54322	+0.99	+0.075	-0.070
III	-7.5676	-1.7427	-0.54361	+0.12	+0.0057	+0.0018
IV	-7.5610	-1.7427	-0.54361	+0.034	+0.0057	+0.0018
HS	-7.6200	-1.7438	-0.54322	+0.81	+0.069	-0.070
MS-MA	-7.6198	-1.7438	-0.54322	+0.81	+0.069	-0.070
HAV	-4.0215	-0.8773	-0.27175	-46.8	-49.7	-50.0
variational	-7.5584	-1.7426	-0.54360	—	—	—

* $\bar{E}_{\text{Coul}}^{\text{var}}$ and \bar{E}_{Coul}^p label respectively the Coulomb energies calculated variationally and perturbationally through the second order

method) give the Coulomb energies also close to each other, but poorer than the values predicted by the methods III and IV. This manifests itself especially at $R = 12$ a. u., where the methods III and IV give the Coulomb energy identical and equal to -0.54361 cm^{-1} , all other methods give the same value -0.54322 cm^{-1} , while the variational Coulomb energy is -0.54360 cm^{-1} . The success of the methods III and IV in the Coulomb energy calculation is connected with the presence of the major part of the Coulomb (R^{-k}) terms in the \mathcal{H}_0 operator.

It is difficult to extrapolate to other molecules the main features of the methods investigated above. It seems, that the conclusions arising from the examination of the exchange and Coulomb energies should be more transferable than those concerning the interaction energies. In the first two cases one calculates the quantities having a quite different functional dependence on R . In the interaction energies the Coulomb and the exchange effects are mixed. If the above supposition is correct, then it seems, that the exchange energy should be calculated by the method I and the Coulomb energy by the methods III or IV.

However, the last two methods require more computational effort than the remaining ones. For larger interacting systems this difficulty may be overcome by using approximations for calculation of integrals. It seems that in perturbational approaches, in the small overlap region, such a possibility exists and the Mulliken approximation may turn out to be an effective one [10]. One can expect, that the Mulliken or more sophisticated approximations, such as those of Löwdin [11] and Cizek [12], should permit applications of the perturbational methods to systems of practical interest.

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