THE ENERGY OF THE INTERACTION BETWEEN TWO ATOMS CALCULATED BY USING THE VARIATIONAL METHOD

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The reasons for the poor numerical accuracy in the variational calculations of the interaction energy between two atoms are investigated. The author presents some possibilities of the improvement of that situation. Some numerical results for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of the hydrogen molecule are given.

Introduction

Very few results of variational calculations for diatomic systems at large internuclear distances have been published till now. Hirschfelder and Linnet [1] have carried out such calculations for H_2 with a very simple trial wave function built up of antisymmetrized products of Slater-type orbitals. A much more accurate energy of the hydrogen molecule at the internuclear distances up to 10 a.u. has been obtained by Kołos and Wolniewicz [2]. In their wave function they used a series of integer powers of the elliptic coordinates and those of the interelectronic distance. The results in the vicinity of the equilibrium distance are excellent, but at large distances the relative accuracy of the interaction energy is much lower because of the rounding errors.

For two helium atoms, variational calculations were carried out by Kim [3] and Moore [4] but, as shown by Kestner and Sinanoglu [5], their results are inaccurate. To the best knowledge of the author, no other variational calculations for large internuclear distances have been published.

A common opinion is that the interaction energy of two atoms at large internuclear distances cannot be determined accurately by the variation method (see *e.g.* the review by Hirschfelder and Meath [6]). For large internuclear distances the interaction energy presented in the papers mentioned above is less accurately calculated than for smaller ones. The objective of the present contribution is to discuss the reasons of such a situation. The possibilities of improving the accuracy of the variational calculations, and some numerical results for H_2, will also be presented.

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Conditions of the accurate calculation of the interaction energy

The variational energy is defined by the formula

$$E = \int \psi^* H \psi d\tau \Big/ \int \psi^* \psi d\tau \tag{1}$$

where H and ψ is the Hamiltonian and the trial wave function, respectively.

Let

$$\psi = \sum_m a_m \cdot f_m \tag{2}$$

where f_m are the linearly independent normalized basis functions and a_m — the variational parameters in the linear combination[1].

Then

$$E = \sum_{m,j} a_m a_j H_{mj} \Big/ M \tag{3}$$

where

$$M = \sum_{m,j} a_m a_j S_{mj}$$

$$H_{mj} = \langle f_m | H | f_j \rangle; \quad S_{mj} = \langle f_m | f_j \rangle.$$

If we retain in the sum (2) only one basis function, say f_1, the energy (3) would be equal to $E_1 = H_{11}/S_{11}$. It can be easily seen that

$$E - E_1 = \sum_{m,j}{}' a_m a_j (H_{mj} - E_1 S_{mj}) \Big/ M \tag{4}$$

where the symbol indicates that the identically vanishing term $a_1^2(H_{11} - E_1 S_{11})$ has to be omitted in the summation.

If H_{11} is the lowest one among all H_{mk}, and the a_j coefficients are in their absolute value by a few orders of magnitude smaller than a_1, then the term $a_1^2 H_{11}/M$ in Eq. (3) is in its absolute value much greater than every other term, and much greater than $E - E_1$. There is no such a term in the formula (4). Therefore, the value $E - E_1$ can be calculated much more accurately by Eq. (4) than the total energy calculated by Eq. (3), especially when functions f_m are orthogonal or almost orthogonal.

Now, let us consider two interacting atoms A and B. The energy of the interaction between these atoms is $E_{\text{int}} = E(AB) - E(A) - E(B)$, where $E(AB)$ is the energy of the diatomic system AB at the distance R between the nuclei, and $E(A)$, $E(B)$ — the energies of the separate atoms. For the hydrogen-like atoms the accurate energies are known, but for the other ones and all molecules the energies $E(A)$, $E(B)$, have to be calculated by using some approximate wave functions. The accuracy of the interaction energy, E_{int}, depends considerably on the choice of the approximations. It is well known, that at internuclear distances so large that the interatomic overlap can be neglected, E_{int} can be determined by the perturbational method in the polarization approximation (see *e.g.* the paper by Kołos [7]). If in a variational method such a basis of approximate wave functions is adopted which guaranties that the resulting E_{int} for very large internuclear distances would

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[1] It is assumed for the sake of simplicity of the notation, that the functions f_m are real. All conclusions remain valid also in the case of complex functions f_m.

approach the results of the perturbational method mentioned above, the discussion of the results will be much easier. Let us consider an example of such a basis.

Let the Hilbert spaces $\{\varphi_A^i\}$ and $\{\varphi_B^j\}$ correspond to the atoms A and B, respectively. The Cartesian product of these Hilbert spaces $\{\varphi_A^i\} \times \{\varphi_B^j\}$, is also a Hilbert space. In practice the number of the basis functions used in the atomic and molecular calculations is limited. Let this number be m for atom A and q for atom B. Let us denote the basis functions of the Hilbert space $\{\varphi_A^i\}$ by $u_1 \ldots u_i \ldots u_m$ and for space $\{\varphi_B^j\}$ by $w_1 \ldots w_j \ldots w_q$. Let atom A have n_A electrons, atom $B - n_B$ electrons. The u functions are the antisymmetric functions of the electrons $1, 2, \ldots n_A$ and the w functions — of the electrons $n_A+1, n_A+2, \ldots n_A+n_B$. The basis functions of the $\{\varphi_A^i\} \times \{\varphi_B^j\}$ space are $u_i(1 \ldots n_A) w_j(n_A+1 \ldots n_A+n_B)$. Let $\boldsymbol{A}$ be such an operator that all the functions $\boldsymbol{A} u_i(1 \ldots n_A) w_j(n_A+1 \ldots n_A+n_B)$ are antisymmetric with respect to the permutation of any two electrons. Let us accept the set $\boldsymbol{A} u_i w_j$ as the basis set in order to calculate the approximate wave function of AB molecule. We assume that m and q are sufficiently small so that no linear or quasilinear dependencies appear.

For the lowest state of a given symmetry and large internuclear distances a good approximation to the wave function can be obtained by using the function $\boldsymbol{A} u^0 w^0$ where u^0, w^0 are the approximate wave functions for the corresponding states of the atoms A and B, respectively. If u^0 and w^0 belong to the space $\{\varphi_A^i\}$ and $\{\varphi_B^j\}$ respectively, then the function $\boldsymbol{A} u^0 w^0$ belongs to the space $\{\varphi_A^i\} \times \{\varphi_B^j\}$. If u_i and w_j satisfy the condition $\langle \boldsymbol{A} u_i w_j | \boldsymbol{A} u^0 w^0 \rangle \neq 0$ we can replace one of our basis functions $\boldsymbol{A} u_i w_j$ by $\boldsymbol{A} u^0 w^0$. Now let us label the functions of our new basis by $f_1, f_2, \ldots f_{mq}$ in such a way that $f_1 = \boldsymbol{A} u^0 w^0$. The variational wave function of a molecule is given is this basis as $\psi = \sum_j a_j f_j$.

For the ground state (or the lowest state of a given symmetry) and large internuclear distances the function f_1 is a leading one among all f_j, so that $|a_1| \gg |a_j|$ for $j \neq 1$. Therefore in order to improve the accuracy of the calculation of $E - E_1$, the formula (4) can be used.

It is evident that if the internuclear distance, R, tends to infinity, then $E_1 = H_{11}/S_{11}$ tends to $E_A + E_B$ where $E_A + E_B$ is the sum of the atomic energies calculated by using u^0 and w^0 wave functions, respectively. Therefore the energy of the molecule at large R is calculated with similar accuracy as the energies of the separate atoms. If we neglect in our basis functions $\boldsymbol{A} u_i w_j$ the "interatomic" antisymmetrization due to the operator $\boldsymbol{A}$, we obtain the basis used in the perturbational calculations in the polarization approximation [7]. Since at large R the "interatomic" overlap and antisymmetrization can be neglected, the variational interaction energy E_{int}, calculated by using the basis $\boldsymbol{A} u_i w_j$ should be very close to the result of the "polarization" perturbational calculation, W_{int}.

The value of $E_{\text{int}} = E(AB) - E(A) - (EB)$ can be calculated as follows

$$E_{\text{int}} = (E(AB) - E_1) + (E_1 - E(A) - E(B)). \tag{5}$$

In the cases discussed above the term $E(AB) - E_1$ can be calculated by the formula (4) without loss of accuracy. The term $E_1 - E(A) - E(B)$ can be calculated accurately if f_1 is of the type $\boldsymbol{A} u^0 w^0$ and if the two-centre integrals are calculated in a way presented below. The two-centre two-electron integrals are clasified as the Coulomb, hybrid and exchange integrals. The hybrid and exchange integrals behave at large internuclear distances like

$R^n \exp(-bR)$ where b is the sum of the appropriate orbital exponents. The Coulomb integrals

$$C = \int \psi_i(\boldsymbol{r_{1A}}) \psi_j(\boldsymbol{r_{1A}}) |r_{12}^{-1}| \psi_k(\boldsymbol{r_{2B}}) \psi_l(\boldsymbol{r_{2B}}) d\boldsymbol{r_1} d\boldsymbol{r_2}$$

behave like R^{-n} similarly as the G integrals

$$G = \int \psi_i(\boldsymbol{r_A}) |r_B^{-1}| \psi_j(\boldsymbol{r_A}) d\boldsymbol{r}.$$

For large R the sum of the respective C and G integrals is by a few orders of magnitude smaller than their absolute values and loss of significant digits occurs during the summation. However, if basis functions of the type $Au_i w_j$ and u_i, w_j are built up of Slater-type orbitals, we can avoid this trouble. In such a case we can find for C and G integrals the expansion $J_k = \sum_m c_{km} R^{-m} + g_k(R)$ where J_k stands for C or G integral and $g_k(R)$ behaves at large R like $R^n \exp(-bR)$. The coefficients c_m are functions of the orbital exponents and of the quantum numbers characterizing the Slater-type orbitals. The sum of such two integrals is given as

$$J_1 + J_2 = \sum_m (c_{1m} + c_{2m}) R^{-m} + (g_1(R) + g_2(R)).$$

The coefficients c_{km} can be tabulated. If some c_{1m} are equal to $-c_{2m}$ they cancel each other in the algorithm and do not decrease the numerical accuracy.

Now let us discuss some conditions of accurate calculation of the expression $E - E_1$ from Eq. (4). The result is accurate if f_1 is the most important among all the basis wave functions f_m and if the basis is well defined $i.e.$ if there are no linear or quasilinear dependencies among f_m at large R. The last condition is equivalent to the condition that the overlap integral matrix $\boldsymbol{S}$ exists and is non-singular. In particular the matrix $\boldsymbol{S}_\infty = \lim_{R \to \infty} \boldsymbol{S}$ should be non-singular. It can be shown that the basis in the elliptic coordinates used $e.g.$ by Kołos and Wolniewicz [2] does not fulfil this condition.

Let us consider two such basis functions f_i and f_j where $e.g.$

$$f_i = N_i \exp[-\alpha(\xi_1 + \xi_2)] \begin{Bmatrix} \cosh \\ \sinh \end{Bmatrix} [\beta(\eta_1 - \eta_2)] \, \xi_1^{r_i} \eta_1^{s_i} \times$$

$$\times \xi_2^{\bar{r}_i} \eta_2^{\bar{s}_i} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (m_i \varphi_1) \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (\bar{m}_i \varphi_2) \tag{6}$$

ξ_1, η_1, φ_1, ξ_2, η_2, φ_2 are the elliptic coordinates of the electrons 1 and 2, respectively, α, β — the orbital exponents, r_i, s_i, m_i, $\bar{r}_i$, $\bar{s}_i$, $\bar{m}_i$ — positive integers or zero, N_i — the normalization coefficient. The normalization coefficient N_i and the overlap integral $\langle f_i | f_j \rangle$ can be easily calculated. The results are

$$N_i = (\pi R^3/16)^{-1} \{2(1 + \delta(m_i, 0))(1 + \delta(\bar{m}_i, 0))\}^{-1/2} \times$$

$$\times \{(B(2s_i, 2\beta) A(2r_i + 2, 2\alpha) - B(2s_i + 2, 2\beta) A(2r_i, 2\alpha)) \times$$

$$\times (B(2\bar{s}_i, 2\beta) A(2\bar{r}_i + 2, 2\alpha) - B(2\bar{s}_i + 2, 2\beta) A(2\bar{r}_i, 2\alpha)) \pm$$

$$\pm (B(2s_i, 0) A(2r_i + 2, 2\alpha) - B(2s_i + 2, 0) A(2r_i, 2\alpha)) \times$$

$$\times (B(2\bar{s}_i, 0) A(2\bar{r}_i + 2, 2\alpha) - B(2\bar{s}_i + 2, 0) A(2\bar{r}_i, 2\alpha))\}^{-1/2} \tag{7}$$

and

$$\langle f_i | f_j \rangle = N_i N_j (\pi R^3/16)^2 \delta(m_i, m_j) \delta(\overline{m}_i, \overline{m}_j) \delta(\sin, \cos) \times$$
$$\times (1 + \delta(m_i, 0))(1 + \delta(\overline{m}_i, 0))\{((-1)^{s_i + s_j} + (-1)^{\overline{s}_i + \overline{s}_j}) \times$$
$$\times (B(s_i + s_j, 2\beta)A(r_i + r_j + 2, 2\alpha) - B(s_i + s_j + 2, 2\beta)A(r_i + r_j, 2\alpha)) \times$$
$$\times (B(\overline{s}_i + \overline{s}_j, 2\beta)A(\overline{r}_i + \overline{r}_j + 2, 2\alpha) - B(\overline{s}_i + \overline{s}_j + 2, 2\beta)A(\overline{r}_i + \overline{r}_j, 2\alpha)) \pm$$
$$\pm 2(B(s_i + s_j, 0)A(r_i + r_j + 2, 2\alpha) - B(s_i + s_j + 2, 0)A(r_i + r_j, 2\alpha)) \times$$
$$\times (B(\overline{s}_i + \overline{s}_j, 0)A(\overline{r}_i + \overline{r}_j + 2, 2\alpha) - B(\overline{s}_i + \overline{s}_j + 2, 0)A(\overline{r}_i + \overline{r}_j, 2\alpha))\} \tag{8}$$

where A and $\overline{B}$ are the standard integrals

$$A(m, z) = \int\limits_1^\infty t^m \exp(-zt)dt$$

$$B(m, z) = \int\limits_{-1}^1 t^m \exp(-zt)dt$$

and $\delta(m_i, m_j)$ or $\delta(\sin, \cos)$ stand for the Kronecker delta symbols. The $\pm$ symbol in Eqs (7) and (8) means that if sinh and sin functions are used in Eq. (6) instead of cosh and cos functions, the minus sign will be used instead of the plus sign.

Now let us assume that $m_i = m_j$, $\overline{m}_i = \overline{m}_j$, $s_i = s_j$, $\overline{s}_i = \overline{s}_j$, but $r_i \neq r_j$ and $\overline{r}_i \neq r_j$. In such a case all the B integrals in the expression for $\langle f_i | f_j \rangle$ (Eq. (8)) are equal to the respective B integrals in the expressions for N_i, N_j (Eq. (7)). The respective A integrals are different. However, they fulfil the relation

$$A(m, z) = A(0, z)(1 + m/z + \ldots + m!/z^m). \tag{9}$$

It can be seen from Eq. (9) that if the argument z, which in our case is proportional to the internuclear distance R, is very large, the relative differences $(A(m, z) - A(p, z))/A(m, z)$ where m and p are arbitrary natural numbers, are very small, especially if m and p are small. They tend to zero as R tends to infinity. As a result, the overlap integrals $\langle f_i | f_j \rangle$ tend to 1 and the basis becomes linearly dependent.

If the basis is composed of the $Au_i w_j$ functions *i.e.* the antisymmetrized products of the *atomic* wave functions, the matrix $\mathbf{S}_\infty$ is well defined. Such a basis is used in the present calculations.

Method of calculation

The numerical calculations have been carried out for the hydrogen molecule. In this case the molecular wave function can be factorized into its space and spin parts. Since our Hamiltonian does not contain spins, we can consider as our basis f functions only the space parts of $Au_j w_p$ functions. This typical f function is given as

$$f_i = N_i \mathbf{A}(\psi_i(a1)\psi_{\overline{i}}(b2) \pm \psi_i(b1)\psi_{\overline{i}}(a2)) \tag{10}$$

where $\mathbf{A}$ denotes symmetrization or antisymmetrization with respect to permutation of the electrons for singlet and triplet states, respectively. The $+$ or $-$ sign in (10) determines the g or u symmetry, respectively, for Σ states, and u or g symmetry for π states. The $\psi_i(cn)$

denote the atomic orbitals of the electron n centered on atom c. The positive direction of the z-axis for each atom is taken toward the other atom. N_i is the normalization coefficient.

The exact eigenfunction of the complete clamped nuclei Hamiltonian can be represented [7] by an expansion in terms of the functions (10). The matrix element $S_{\infty ij} = \lim_{R \to \infty} \langle f_i | f_j \rangle$ is given by the formula

$$S_{\infty ij} = \{(1 + |\langle \psi_i | \psi_{\bar{i}} \rangle|^2)(1 + |\langle \psi_j | \psi_{\bar{j}} \rangle|^2)\}^{-1/2} \times$$
$$\times (\langle \psi_i | \psi_j \rangle \langle \psi_{\bar{i}} | \psi_{\bar{j}} \rangle + \langle \psi_i | \psi_{\bar{j}} \rangle \langle \psi_{\bar{i}} | \psi_j \rangle). \tag{11}$$

The ψ orbitals used were the normalized real Slater-type orbitals with common orbital exponent

$$\Psi_{nlm}(r, \vartheta, \varphi) = \{2^{2n+1} \pi^{-1}/(2n)!\}^{1/2} r^{n-1} \times$$
$$\times \exp(-\alpha r) \left\{ \left(l + \frac{1}{2}\right)(l - |m|)!/(l + |m|)! \right\}^{1/2} (2^l l!)^{-1} \times$$
$$\times (\sin \vartheta)^{|m|/2} \frac{d^{l+|m|}}{d \cos \vartheta^{l+|m|}} (\cos^2 \vartheta - 1)^l (1 + \delta_{m,0})^{-1/2} \times$$
$$\times \begin{cases} \cos(m\varphi) & \text{if } m \leqslant 0 \\ \sin(m\varphi) & \text{if } m > 0. \end{cases} \tag{12}$$

In contrast to the hydrogenic orbitals the set of such orbitals is complete in the discrete spectrum. For the orbital exponent the asymptotic value $\alpha = 1$ was assumed.

The Coulomb integrals were calculated by the method of Fourier transforms and recursive formulas [8, 9]. A similar method has ben independently developed by Harris [10, 11]. The exchange integrals were calculated by the method of Harris and Michels [8] and the one-electron integrals by the method of the expansion in elliptic coordinates using the program of Szondy [12].

Numerical calculations were carried out for the lowest $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states. The variational coefficients a_m in expansion (2) were obtained by using the diagonalization procedure of Ostrowski [13–15] modified in the following way. After the calculation of all the a_m coefficients in one iteration the energy for the next iteration was calculated as $E = E_1 + (E - E_1)$ where $E - E_1$ was given by Eq. (4). This modification improved the accuracy of the Ostrowski procedure.

The Ostrowski method is not the most accurate for the calculation of a_j. More accurate is the method of Roothaan and Bagus [16]. It is worth while to mention that similar accuracy can also be achieved by using a simpler method proposed by the present author. This method is given in the Appendix.

The interaction energy, E_{int}, was calculated from the formulas (5) and (4), and the term $E_1 - E(A) - E(B)$ as

$$E_1 - 2E(H) = (1 \pm s^2)^{-1}\{\pm(L - s \exp(-R)(5R/3 - 1 + R^{-1})) -$$
$$- \exp(-2R)(R^2/6 + 3R/4 - 5/8 - R^{-1})\} \tag{13}$$

where L and s are the exchange and overlap integrals, respectively,

$$L = \int \psi_1(a1)\psi_1(b1)(1/r_{12})\psi_1(a2)\psi_1(b2)d\mathbf{r}_1 d\mathbf{r}_2$$
$$s = \int \psi_1(a1)\psi_1(b1)d\mathbf{r}_1$$

the symbol ψ_1 denotes the 1s orbital and the $+$ or $-$ sign has to be used for singlet and triplet state, respectively. The formula (13) can be derived from the formulas for the respective integrals published by Hirschfelder and Linnett [1].

Numerical calculations were performed on the GIER computer at the Computer Centre of the University of Warsaw. They were carried out for $^1\Sigma_g$ and $^3\Sigma_u$ states at two internuclear distances $R = 8$ and $R = 10$ a.u. The configurations $1s1s$, $2p2p$, $2p3p$, $2p3d$, $2p_0 4f_0$, $3d_0 3d_0$ were used in the expansion.

The variational energy was calculated for both values of R by Kołos and Wolniewicz [2], and for $R = 8$ the values of E_int determined by various perturbational methods were also published by Certain et al. [17]. Therefore the comparison of all these results with the present values of E_int for $R = 8$ a.u. could be a good test of the accuracy of the present method.

The basis of Kołos and Wolniewicz was not satisfactory at very large R as shown in the preceding section. On the other hand, the present basis should be more advantageous for large than for small internuclear distances. Therefore it was interesting to see if the accuracy of the present basis could be comparable with that of Kołos and Wolniewicz at any value of R for which their calculations had been carried out. The present calculations were carried out just at $R = 10$ a.u. because it was the largest among such values.

For internuclear distances such as 8 or 10 a.u. the discussed above cancellations of C and G integrals in the Hamiltonian matrix elements other than $H_{11} = \langle f_1 | \boldsymbol{H} | f_1 \rangle$, did not decrease the numerical accuracy of the resulting E_int. The formula (13), which determines $E_1 - E(A) - E(B) = H_{11}/S_{11} - 2E(H)$ or the so called Heitler-London correction, is free from cancellations. As a result, no such effects decreased the numerical accuracy of the E_int.

Results and discussion

Numerical results are collected in the Tables I and II. In Table I we show the negative values of the interaction energy, E_int, exchange energy, E_ex, Coulomb energy, C and the Coulomb energy calculated by Kołos [7] using the perturbation method in the polarization approximation, denoted by CP. All values are in cm^{-1}. The label singl. refers to $^1\Sigma_g^+$ state and tripl. — to $^3\Sigma_u^+$ state. The number Nf means the number of terms in the trial wave function (2). For $1s1s, 2p2p, 2p3p, 2p3d, 2p_0 4f_0, 3d_0 3d_0$ configurations we have $Nf = 12$, for $1s1s, 2p2p, 2p3p, 2p3d, 2p_0 4f_0 - Nf = 11$, for $1s1s, 2p2p, 2p3p, 2p3d - Nf = 10$, for $1s1s, 2p2p, 2p3p - Nf = 7$, for $1s1s, 2p2p - Nf = 4$ and for $1s1s$ configuration or the Heitler-London wave function — $Nf = 1$. The wave functions representing the configurations $2p_1 2p_1$ or $2py2py$ and $2p_{-1}2p_{-1}$ or $2p_x 2p_x$ etc. are treated as independent f_m functions for the convenience in programming. The exchange and Coulomb energies are defined as

$$E_\text{ex} = \frac{1}{2} \left(E_\text{int}(^1\Sigma_g^+) - E_\text{int}(^3\Sigma_u^+) \right)$$

$$C = \frac{1}{2} \left(E_\text{int}(^1\Sigma_g^+) + E_\text{int}(^3\Sigma_u^+) \right).$$

TABLE I

Interaction energies in cm^{-1}

	Nf	$-E_{int}$		$-E_{ex}$	$-C$	$-CP$	$-E_{est}$	
		singl.	tripl.				singl.	tripl.
$R = 8$ a. u.	1	3.818	−3.032	3.424	0.393	0	3.82	−3.50
	4	8.817	1.873	3.472	5.345	5.024	8.84	1.52
	7	9.179	2.181	3.499	5.680	5.410	9.23	1.91
	10	10.603	3.527	3.538	7.066	6.923	10.75	3.42
	11	10.787	3.708	3.540	7.248			
	12	10.859	3.774	3.543	7.317			
	ap			3.66		7.740	11.56	4.24
	KW	11.6	4.3	3.65	7.95			
$R = 10$ a. u.	1	0.113	−0.092	0.103	0.011	0	0.11	−0.12
	4	1.430	1.221	0.105	1.326	1.317	1.43	1.20
	7	1.530	1.316	0.107	1.423	1.418	1.53	1.30
	10	1.786	1.567	0.109	1.676	1.672	1.79	1.55
	11	1.812	1.594	0.109	1.703			
	12	1.822	1.602	0.110	1.712			
	ap			0.117		1.771	1.88	1.65
	KW	2.0	1.5	0.25	1.75			

TABLE II

Expansion coefficients $a_j \cdot 10^4$

j	conf.	a_j, $R = 8$ a.u.		a_j, $R = 10$ a.u.	
		singl.	tripl.	singl.	tripl.
1	$1s1s$	−10000	−9994.9	−10000	−9999.9
2	$2p_0 2p_0$	15.5777	11.3207	6.2596	6.0424
3	$2p_1 2p_1$	7.5629	8.4152	3.0521	3.1003
4	$2p_{-1} 2p_{-1}$	7.5629	8.4152	3.0521	3.1003
5	$2p_0 3p_0$	26.6091	31.8920	15.9764	16.1973
6	$2p_1 3p_1$	13.9844	12.8179	8.1013	8.0376
7	$2p_{-1} 3p_{-1}$	13.9844	12.8179	8.1013	8.0376
8	$2p_0 3d_0$	17.4118	17.9123	7.6980	7.6820
9	$2p_1 3d_1$	10.9957	10.4056	4.4738	4.4430
10	$2p_{-1} 3d_{-1}$	10.9957	10.4056	4.4738	4.4430
11	$2p_0 4f_0$	8.0362	8.2230	3.0230	2.9768
12	$3d_0 3d_0$	4.9984	4.7858	1.8976	1.8383

The values of Kołos and Wolniewicz [2] are written in the row denoted by KW. In the row denoted by ap the values of the asymptotic exchange energy calculated by Herring and Flicker [18] as well as the three-term (up to R^{-10}) CP energies [7] are given. The meaning of the columns E_{est} will be given below.

The results show that $-E_{exch}$ increases slightly with the number of basis functions, Nf, being in all cases a little smaller than the Herring-Flicker energy, E_{exas}. The differences between these two energies are small for both internuclear distances. The results of Kołos

and Wolniewicz agree very well with those of Herring and Flicker at $R = 8$ a.u., but at $R = 10$ a.u. the results disagree in spite of the fact that E_{exas} should be more accurate at $R = 10$ a.u. than at smaller internuclear distances. This disagreement is probably due to the discussed above inaccuracy of the Kołos–Wolniewicz basis at large R. Since the present E_{ex} for $Nf = 12$ agrees at both R very well with E_{exas} and the triplet energy is at $R = 10$ a.u. lower than the KW value, the accuracy of the present results is at $R = 10$ a.u. probably greater than that of Kołos and Wolniewicz. For such internuclear distances as $R = 8$ a.u. the KW results are considerably lower and much more accurate than the present energies.

It is interesting to note that the energies of the singlet state at 10 a.u. are almost equal to the sum of the perturbation dispersion energies CP calculated with the same number of terms plus the Heitler-London energy E_1^i. This fact can be explained as follows. For singlet state of H_2 molecule the basis of unsymmetrized products $u_i w_j$ atomic configurations is complete if all the configurations are taken into account. The $\boldsymbol{S}$ matrix of the overlap integrals as well as the $\boldsymbol{H}$ matrix of the Hamiltonian defined in the antisymmetrized $\boldsymbol{A} u_i w_j$ basis, except H_{11}, are for large R very close to the respective matrices defined in the unsymmetrized basis $u_i w_j$, e.g., the present calculations have shown that the differences between respective matrices are very small at $R = 10$ a.u. The considerable difference in the H_{11} matrix element is equal to the Heitler-London correction. As a result, if a new configuration is taken into account in the $\boldsymbol{A} u_i w_j$ basis, the improvement of the energy is almost the same as that made by the same configuration in the unsymmetrized $u_i w_j$ basis. Therefore the difference between these two bases for the respective number of configurations is almost equal to the Heitler-London correction.

As a result, we can obtain an estimate of the singlet E_{int} for given Nf as the sum of the Heitler-London correction plus the respective CP energy. This sum is given as E_{est} for the singlet state. For the triplet state we can make use of the fact that the exchange energy E_{ex} is very close to the Herring-Flicker E_{exas} and obtain the E_{est} by subtracting $2E_{exas}$ from E_{est} for the singlet state. Such estimates are given as E_{est} for the triplet state. For the asymptotic values of E_{est} (the row ap) the value of CP presented in the row ap is used. These values of E_{est} are at $R = 8$ a.u. very close to the KW results. The values of E_{est} as well as the results of the present variational calculations suggest that the exact values of the interaction energy at $R = 10$ a.u. are not lower than -2.0 cm^{-1} and -1.75 cm^{-1} for the singlet and triplet state, respectively.

The variational coefficients a_j of the expansion (2) are given for $Nf = 12$ in Table II. All the basis functions f_m as well as the trial wave function ψ are normalized to 1. The a_1 coefficients are rounded off up to 5 significant digits. The a_1 coefficients used in order to calculate E_{int} are -1.00001550, -0.999948762 for the singlet and triplet states at $R = 8$ a.u. and -0.999996992, -0.999994615 for the singlet and triplet states at $R = 10$ a.u., respectively.

It can be seen that the absolute values of all the coefficients other than a_1 are by at least three orders of magnitude smaller than $|a_1| \approx 1$. It should also be noted that $|H_{11}|$ is much greater than the absolute values of other Hamiltonian matrix elements. As a result, there is no loss of accuracy in the algorithm (4).

The present values of the E_{int} at $R = 8$ a.u. are in a good agreement with recent Piela's perturbational results [19, 20]. Piela also used the basis Au_iw_j and the Slater-type orbitals with the common orbital exponent equal to 1. Some matrix elements were neglected in his calculations. His basis contained the same configurations as the present one except the $2p_04f_0$, and besides many others. The lowering of the E_{int}, due to these other configurations, was at $R = 8$ a.u. a little greater in the singlet state and almost the same in the triplet state than the lowering due to the $2p_04f_0$ configuration in the present calculations. This proves that the $2p4f$ configuration is very important at such internuclear distances as $R = 8$.

Certain *et al.* [17] used the same basis as Kołos and Wolniewicz [2]. Among their results only those of the HS and HAV method (for the meaning of the abbreviations see paper [17]) were closer to the KW results than the present values of E_{int}.

Concluding: The present contribution proves that the interaction energy can be calculated with a good numerical accuracy by using the variational method, and proposes the basis set along with the algorithms fitting that purpose.

APPENDIX

A simple modification of the Ritz variational method

Let us consider a system of n basis functions f_m and let f_1 be the most important among these functions in the problem under consideration *i.e.* in Eq. (2) the variational coefficients $|a_m| \ll |a_1|$ for $m \neq 1$. The variational coefficients A_1 and A_2 in the wave function $\varphi_{12} = A_1f_1 + A_2f_2$ can be calculated by the Ritz method. After this calculation the function φ_{12} can be combined with f_3, resulting in the function φ_{13}. The functions $\varphi_{14}, \ldots \varphi_{1n}$ where *e.g.* $\varphi_{1k} = \sum_{j=1}^{k} a_{ij}f_j$ can be obtained in a similar manner. Then the process can be repeated. The functions $f_2, f_3, \ldots f_n$ can again be introduced in the linear combination and the approximate wave functions $\varphi_{22}, \varphi_{23}, \ldots \varphi_{2n}$ can be obtained. In such a way the 3-rd, 4-th iteration *etc.* can be made until sufficient accuracy of the energy and of the coefficients a_j is reached.

Details of the linear combination of two functions, say g_1 and g_2 will now be presented. The secular equation

$$\det \{H_{kj} - ES_{kj}\} = 0 \quad \text{where } k, j = 1, \ldots n$$

is for $n = 2$ the simple algebraic equation of the kind $az^2 + bz + c = 0$. In our case $b^2 - 4ac = (h_{22} - h_{11})^2(1 + W)$ where

$$W = 4(h_{12} - sh_{11})(h_{12} - sh_{22})(h_{22} - h_{11})^{-2}$$

$$s = \langle g_1|g_2 \rangle \quad \text{and} \quad h_{jk} = \langle g_j|H|g_k \rangle.$$

If $|W| < 1$ then $(1+W)^{1/2}$ can be expanded in the power series and after some manipulations the following expression for the lowest energy E can be obtained.

$$E - h_{11} = -\{1/(1-s^2)\} \times \{(h_{12} - sh_{11})^2)/(h_{22} - h_{11})\} \times$$

$$\times \{1 - \{(h_{12} - sh_{22})/(h_{22} - h_{11})\}^2 \times \{1 + 8W \sum_{n=3}^{\infty} ((-W)^{n-3}(2n-3)!!/(2^n n!))\}\}. \tag{A1}$$

Now let g_2 be our basis wave function f_k, $k \geqslant 2$, and $g_1 = \varphi_{m,k-1}$ obtained when f_{k-1} is taken into account in the m-th iteration.

The relation between $h_{12} - sh_{11}$ and some expression of the Ritz method can be easily found.

Namely

$$h_{12} - sh_{11} = \sum_j a_j (H_{kj} - h_{11} S_{kj}). \tag{A2}$$

It is well known that the coefficients a_j are calculated in the Ritz method from the equations

$$r_k = \sum_j a_j (H_{kj} - ES_{kj}) = 0, \quad k = 1, ..., n. \tag{A3}$$

Since h_{11} is an approximation to the variational energy E, the energy lowering $E_{m,k} - E_{m,k-1}$ is approximately proportional to r_k^2 and vanishes only if the corresponding equation (A3) holds. The vector of the coefficients a_k can be calculated at each stage of the iteration process by using numbers A_1 and A_2.

Some illustrative numerical calculations using this method suggest that it is more accurate than the Ostrowski method. It is quickly convergent when the absolute values of the off-diagonal matrix elements are small. If they are not small, the convergence is much slower, but in such a situation a linear extrapolation can be used in order to obtain a_j and the variational energy can be calculated by Eq. (4).

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